Marine Pollution Bulletin 86 (2014) 266–273

Contents lists available at ScienceDirect

Marine Pollution Bulletin

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

Tissue distribution and fate of persistent organic pollutants in Indo-Pacific humpback dolphins from the Pearl River Estuary, China

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ARTICLE INFO

Article history:
Available online 25 July 2014

Keywords:
Persistent organic pollutants
Indo-Pacific humpback dolphin (*Sousa chinensis*)
Pearl River Estuary
Tissue distribution

ABSTRACT

Eleven persistent organic pollutant (POP) compounds including ∑PCBs, ∑DDTs, ∑HCHs, aldrin, mirex, endrin, ∑CHLs, dieldrin, HCB, heptachlor and pentachlorobenzene were measured in the kidney, liver, muscle, melon and other tissues of *Sousa chinensis* stranded on the western coast of the Pearl River Estuary in China during 2007–2013. For most parameters of POPs measured, melon tissues contained the highest mean concentrations with the exception of aldrin, which was higher in the kidney and liver tissues. The concentrations of PCBs, DDTs, heptachlor and endrin in the melon tissue exhibited significant correlations with body length, whereas PCBs and heptachlor also displayed significant regression with age. Our studies showed hepatic concentrations of ∑DDTs, ∑HCHs and mirex in *S. chinensis* were generally higher than those found in cetaceans from other geographic locations. The high levels of POP residues in the testis of one male dolphin suggested an increasing risk of infertility in the species.

1. Introduction

The Pearl River Delta region in Guangdong Province is one of the fastest-developing areas in China and Asia. Anthropogenic activities have resulted in the release of unprecedented amounts of persistent organic pollutants (POPs) into the Pearl River Estuary (PRE) during the last three decades (Guan et al., 2007; Guo et al., 2008, 2009; Mai et al., 2005, 2002). These POPs have adverse effects on the immune and reproduction systems of animals (Lahvis et al., 1995). According to the stockholm convention on persistent organic pollutants (POPs) (UNEP, 2001), the production and use of POPs including aldrin, chlordane, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), mirex, polychlorinated biphenyls (PCBs) and DDT should be eliminated in the assigned countries including China, which ceased DDT production in 2007. Therefore, studies on bioaccumulation and fate of POPs are critical for protecting the local dolphin populations and monitoring the organic contaminants in the PRE ecosystems.

Because they occupying the top trophic level in the marine food chain, long-lived marine mammals can act as a representative indicator for environmental health and contaminant biomonitoring in aquatic ecosystems (Harvell et al., 1999; Lahvis et al., 1995). Indo-Pacific humpback dolphins (*Sousa chinensis*) are one major group of top predators in the PRE and can therefore record POP contamination by bioaccumulation in this region. According to stomach content analyses of stranded Indo-Pacific humpback dolphins in our lab and other studies (Barros et al., 2004), the preferred prey fishes of the dolphins are also consumed by local human populations. Thus, investigation of the POP levels in the dolphins is also important for risk assessment and the protection of human health.

The Indo-Pacific humpback dolphin is protected as one of the first order of rare animals (The National Key Protected Wild Aquatic Animals List) in China and is included in the Convention on International Trade in Endangered Species of Wild Fauna and Flora Appendix I (CITES, 1997). It has also been classified as a 'threatened species' in the International Union for Conservation of Nature and Natural Resources (IUCN) Red List of Threatened Species because it is suffering adverse effects from many human activities. It was estimated that 74.27% of the current population will be lost after three generations (Huang et al., 2012).

Earlier studies have reported high levels of POPs in the blubber of *S. chinensis* individuals from the PRE (Minh et al., 1999; Ramu et al., 2005; Wu et al., 2013), but information on the tissue distribution of POPs in *S. chinensis* is scarce. In ill and starved animals, as the fat reserves in the blubber are mobilized, the concentrations of lipophilic pollutants in other body tissues, particularly the liver, become enriched (Guitart et al., 1996). Therefore, the investigation

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http://dx.doi.org/10.1016/j.marpolbul.2014.07.007
0025-326X/

of contaminants in the liver, kidney and other tissues is of more value for toxicological assessment than those in the blubber. In this study, concentrations of various POPs in the liver, melon, kidney, muscle and other tissues of *S. chinensis* from the PRE, China, were determined. Gender and age-related differences were investigated within the species, and tissue-specific PCB congener profiles were estimated.

2. Methods

2.1. Sampling

Stranded Indo-Pacific humpback dolphins were collected between 2007 and 2013 from the PRE (Fig. 1). Tissue samples from the kidney ($n = 4$), liver ($n = 4$), muscle ($n = 4$) and melon ($n = 11$) were taken during necropsies of freshly dead (code 2) or early moderate decomposition (code 3) carcasses. Samples were stored at −20 °C until further analysis. The total body length of the dolphins was measured as the straight-line length from the tip of the upper jaw to the fluke notch. Sex was determined by external and internal examination. Age was estimated by counting the growth layer groups (GLGs) in the dentine of the teeth (Hohn et al., 1989; Myrck et al., 1983). Animals aged 2–7 years are considered to belong to the juvenile category, and animals of ages greater than 7 are considered adult.

2.2. Sample preparation

All of the tissue samples were freeze-dried for 48 h using a Labconco freeze-drying system. The dried samples were then ground with an automatic agate mortar for 10 min. The prepared samples were stored in refrigeration pipes at −80 °C prior to chemical analyses.

Approximately 0.5 g (wet weight) of the tissue sample was mixed with sodium sulfate and added to a pressurized fluid extraction cell along with 2.5 ng of recovery internal standards [13C-chlorobiphenyl (CB) 141]. The powder was completely transferred into a pre-cleaned cellulose thimble and then extracted with 200 ml of a 3:1 (v:v) mixture of hexane and dichloromethane (DCM) for at least 18 hours in a Soxhlet apparatus. The extract was concentrated to 10 ml with a rotary evaporator. An aliquot (1.0 ml) was taken for the gravimetric determination of the lipid content. The rest of the solution was filtered through a disposable syringe filter disc (0.45 μm in pore size) and further concentrated to 2.0 ml for subsequent purification.

The lipidic material (>500 Å) in the samples was fractionated and removed by gel-permeation chromatography (GPC). The GPC column (2 cm inner diameter) was packed with *Bio-Beads S-X3* and washed with a 1:1 (v:v) mixture of hexane and DCM prior to sample fractionation. The extract (approximately 2 ml) was placed on the top of the column, and a 1:1 (v:v) mixture of hexane and DCM was used as a mobile phase at a flow rate of 3 ml min^{-1}. The first 70 ml of the fraction was discarded, and the following 130 ml fraction, which contained PCBs and organochlorine pesticides (OCPs), was collected. The eluent was concentrated to approximately 2.0 ml and divided into two parts for further clean-up steps.

We adopted two types of chromatography columns for further purification according to Mai et al. (2002) due to the different chemical properties of PCBs and OCPs. For PCBs, a glass column (1 cm i.d.) was packaged from bottom to top with 1 cm of anhydrous sodium sulfate, 10 cm of acidic silica gel, and 1 cm of anhydrous sodium sulfate. For OCPs, a glass column (1 cm i.d.) was packaged from bottom to top with 1 cm of anhydrous sodium sulfate, 6 cm of alumina, 10 cm of silica gel, and 1 cm of alumina. Each column was washed with hexane prior to application. An aliquot (1.0 ml) of preliminary cleanup sample extract was placed on the top of each column and eluted with a 70 ml 1:1 (v:v) mixture of hexane and DCM. The eluate was rotary-evaporated to a volume of 5 ml and further concentrated by evaporation with a gentle nitrogen flow to approximately 500 μl for the next instrumental analyses.

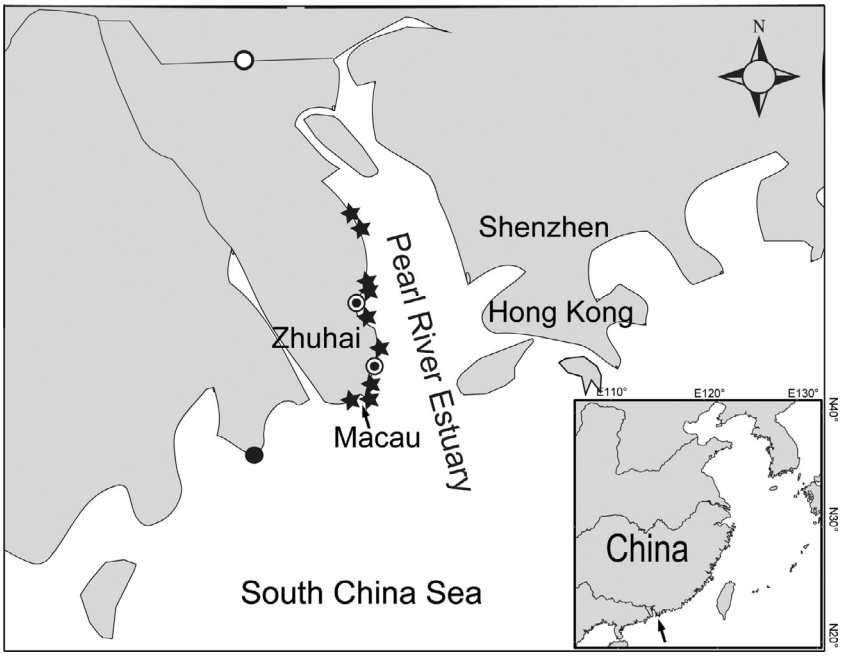

Fig. 1. Sampling locations of stranded Indo-Pacific humpback dolphins from the Pearl River Estuary, China. Five-pointed star (★) denotes the sampled individual whose melon tissue was sampled. Circled dot (⊙) denotes the individual whose melon, liver, kidney and muscle tissues were obtained. Hollowed dot (○) denotes the individual whose liver, kidney and muscle tissues were sampled. The individual humpback dolphin whose muscle, lung, kidney, heart, pancreas, stomach, testis, liver, intestine and blubber tissues were sampled was denoted as solid dot (●).