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Baseline

Levels and trends of polycyclic aromatic hydrocarbons in the Indo-Pacific humpback dolphins from the Pearl River Estuary (2012–2017)

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ABSTRACT

We investigated the levels and trends of the 16 USEPA priority PAHs in the blubber of 37 Indo-Pacific humpback dolphins sampled during the period 2012–2017 from the Pearl River Estuary (PRE), China. Σ_{16} PAHs concentrations (17.6–6080 ng g⁻¹ wet weight) were at median level compared to dolphin species worldwide. Humpback dolphins affiliated with the hotspots of PAHs, had significantly higher levels of Σ_{16} PAHs than individuals from the other areas in the PRE. Moreover, dolphins stranded on the coast of Lingdingyang are significantly more contaminated by Σ_{16} PAHs than those in the West-four region of the PRE, which appears to reflect the heterogeneous distribution of PAHs in the environment. A marked decline in blubber Σ_{16} PAHs levels is observed over the studied period, with the control of a range of confounding factors. The trend is strongly and statistically significant ($p < 0.0001$), indicating that the loading of PAHs are gradually being reduced.

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants, which pose a significant health threat to human and wildlife due to their highly estrogenic, carcinogenic and mutagenic toxicity (Ravindra et al., 2008; Ololade, 2010). PAHs are mainly formed by anthropogenic activities (e.g., petroleum products and sources of the incomplete combustion of organic matter in industrial operations, waste incineration, power plants, vehicle engines and biomass burning). High PAH levels were found in the environment of developing countries, due to the rapid urbanization process in recent years. (Barra et al., 2007; El Deeb et al., 2007; Nikolaou et al., 2009; Kwach and Lalah, 2009). The Pearl River Estuary (PRE), being the second largest river mouth in China in terms of water and sediment discharge, serves the main pathway of terrestrial anthropogenic pollutants to the South China Sea, including PAHs (Yuan et al., 2015). Although many researches have investigated the source, distribution and fate of PAHs in the PRE (Mai et al., 2002; Wang et al., 2007; Yuan et al., 2015), there is a general lack of information of PAH accumulation in higher trophic-level predators. It is widely acknowledged that higher trophic-level aquatic organisms have a certain capacity of metabolizing PAHs. (Nfon et al., 2008; Takeuchi et al., 2009). However, some studies showed that the metabolism ability of PAHs by cetaceans is limited (Fossi et al., 1999). A positive relationship between PAH concentrations in captive killer whale blood samples and dietary intake of fish has been reported

(Formigaro et al., 2014). Therefore, excess intake of PAHs by cetaceans will lead to a bioaccumulation of the pollutant in their blubber.

The PRE harbours the largest population of Indo-Pacific humpback dolphins (*Sousa chinensis*) in the world, which are long-term resident in the PRE year-round (Jefferson and Karczmarski, 2001; Jefferson and Hung, 2004; Chan and Karczmarski, 2017). It has been reported that the number of PRE humpback dolphins may be declining by approximately 2.46% annually, resulting in a reduction of approximately 74% of the current population numbers within three generations of lifespan (about 60 years) (Huang et al., 2012; Karczmarski et al., 2016). As long-term residents and apex predators with a long lifespan, humpback dolphins are vulnerable to bioaccumulation of persistent organic pollutants (POPs) (Bossart, 2011; Fair et al., 2010; Moon et al., 2011). There has been mounting evidence of a link between high accumulation of contaminants and population decline or suppression of population recovery for several cetacean species (Schwacke et al., 2002; Jepson et al., 2016). Regarding the remarkably high ratio of neonatal mortality and immune system abnormalities observed in the stranded dolphins from the PRE, it has long been suspected that anthropogenic contaminants are contributing to the population decline of humpback dolphins in the PRE (Parsons and Jefferson, 2000; Parsons, 2004; Jefferson et al., 2006), which are known to be exposed to an excessively high level of contaminant mixtures, e.g.,

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Dichlorodiphenyltrichloroethanes (DDTs), Polybrominated diphenyl ethers (PBDEs) and butyltin, etc. (Gui et al., 2014; Gui et al., 2017; Parsons, 2004; Ramu et al., 2005; Schwacke et al., 2002; Kajiwara et al., 2006). Significant increasing trends of alternatives of conventional POPs, e.g., hexabromocyclododecane (HBCD) and perfluorobutane sulfonate (PFBS), were reported in the blubber of dolphin and porpoise from Hong Kong waters over the past decade (Yeung et al., 2009; Zhu et al., 2014; Lam et al., 2016; Ruan et al., 2018). However, the baseline data about PAH exposures of the humpback dolphins from the western PRE (west of Hong Kong) is still lacking, despite that one study has reported PAH levels in the humpback dolphins in Hong Kong waters (Leung et al., 2005).

Understanding differences of pollutant exposure in different communities of animals have important implications for risk assessment as well as conservation and management strategies. The main source of PAHs in the PRE is riverine input (Luo et al., 2004; Yuan et al., 2015). The mixing process of riverine input freshwater and marine tidal current can influence the spatial distribution and circulation of PAHs in the PRE, which creates Turbidity Maximum Zone (TMZ) for the deposition of PAHs and other organic pollutants. It is well-documented that the coastal region off Qi'ao Island and Macau are PAH hotspot formed by TMZ, in which the sediments and waters are more contaminated by PAHs than those in any other area in the PRE (Mai et al., 2002; Wang et al., 2007; Luo et al., 2004; Yuan et al., 2015). It is also reported that PAH levels in the west-four region of the PRE is significantly lower than that in the eastern four outlet region (Lingdingyang), due to the marked difference in hydrodynamic conditions between the two main outlet regions. A previous study showed that levels of most halogenated organic pollutants in fish from the PRE have significantly declined from 2008 to 2013, indicating the effectiveness of regulations and source controls in substantively reducing inputs of these contaminants to the PRE (Sun et al., 2015). However, whether these changes can influence PAH levels in the PRE humpback dolphins is still unknown. Significant temporal trends in PAH burdens have been reported in marine vertebrates, mainly after a large amount of petroleum was discharged into marine systems due to the oil spill (Marsili et al., 2001), while no study has reported the time trend of PAH burden in the PRE humpback dolphins. The present study assessed the concentrations of the 16 United States Environmental Protection Agency (USEPA) prior PAHs in the blubber of stranded humpback dolphins collected from the PRE during 2012–2017. Generalized additive mixed models (GAMs) were fitted to the data to test for possible temporal trends and whether the temporal trend is confounded by region, age class, sex, body length and lipid content. To our knowledge, this is the first study of temporal trend of PAH levels in cetaceans from the PRE.

Blubber samples were obtained from 37 Indo-Pacific humpback dolphins that were stranded between 2012 and 2017 from the PRE (Fig. 1) within the collaborative stranding program run by the Guangdong Pearl River Estuary Chinese White Dolphin Reserve, Guangdong Jiangmen Chinese White Dolphin Provincial Nature Reserve and Sun Yat-Sen University. The states of decomposition for the stranding dolphin carcasses were defined using the protocols described in Law et al. (2006). All humpback dolphins used in this study were freshly dead (code 2) or moderately decomposed (code 3). Sex was determined by observing the reproductive organs, and if sex could not be determined in the field, it was determined by DNA analysis. The sexual maturity of the animals was determined by examining the reproductive organs. According to Jefferson et al. (2012), physical maturity of the Indo-Pacific humpback dolphins occurs at lengths between approximately 238 and 249 cm, while calves had body lengths of < 130 cm. Therefore, the adult humpback dolphins were categorized as individuals with body lengths 238 cm and longer and calves with body lengths 130 cm and shorter. Blubber samples were firstly packed in aluminum foil and then placed in clean plastic storage bags and frozen at -80°C for further analysis.

The analyzed compounds were the 16 USEPA prior PAHs, including

naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorine (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (InP), dibenzo[*a,h*]anthracene (DBaA) and benzo[*g,h,i*]perylene (BghiP).

The analytical procedures followed those described in Mai et al. (2002) and Leung et al. (2005). Approximately 0.5 g of a blubber sample was mixed with anhydrous Na_2SO_4 , spiked with 2.5 ng of each recovery internal standard (naphthalene- d_8 , acenaphthene- d_{10} , phenanthrene- d_{10} , chrysene- d_{12} , and perylene- d_{12}), and then extracted with 3:1 (v:v) hexane:dichloromethane (DCM) in an automated Soxhlet apparatus. Subsequently, the extract was evaporated to 10 mL, in which an aliquot (1.0 mL) was taken for gravimetric determination of the lipid content, while the rest of the extract was subjected to purification by BioBeads SX-3-packed gel permeation chromatography (GPC) using a 1:1 (v:v) mixture of hexane:DCM as the eluent at a constant flow rate of 3 mL min^{-1} . The first 70 mL of the eluent, which contained most of the lipids, was discarded. The following 130 mL volume, which contained all the target analytes that were co-extracted with the fat, was collected. The eluent obtained in the last step was evaporated to approximately 2.0 mL and was further purified by passing through a glass column (1 cm i.d.) packed 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. A known quantity of internal standards (*m*-terphenyl- d_{14}) were added to the final eluate prior to instrumental analysis. The target 16 USEPA PAHs were analyzed using a gas chromatograph (GC, Agilent 7890, USA) coupled with a capillary column (DB-5MS with dimensions $60\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$) (J&W Scientific, USA) and a mass spectrometer (MS) detector (Agilent 5975, USA) in electronic ionization mode (EI) with selected-ion monitoring (SIM) acquisition. The GC was operated in the splitless injection mode using $1\text{ }\mu\text{L}$ injection volumes. The column oven temperature for the detection of PAHs was programmed as follows: 70°C held for 2 min, increased at 15°C per minute to 180°C and held for 2 min, increased at 5°C per minute to the final temperature of 240°C and held for 2 min, and increased at 3°C per minute to the final temperature of 315°C and held for 2 min. The temperatures of the transfer line, injector interface, and ion source were set at 300°C , 290°C and 230°C , respectively. Helium was used as the carrier gas. The flow rate was set at 1.0 mL min^{-1} .

All data were subjected to strict quality assurance/quality control (QA/QC). An internal calibration method with five-point calibration curves is used for the quantitative determination of individual PAHs. A method blank, a blank sample spiked with a known standard solution, a matrix spike sample (a known amount of target analyte standard solution spiked into pre-extracted blubber), and a sample duplicate in every batch of 10 samples were analyzed together with our samples. The relative standard deviation (RSD) for the repeated samples is < 5%. The concentrations in the procedural blanks never exceeded the three-fold values of the method detection limit (MDL), which ranged from 0.35 ng g^{-1} wet weight (ww) to 4.5 ng g^{-1} ww for all analyzed individual compounds. The relative difference between duplicate samples was below 15% for all target analytes. Recovery of surrogate internal standards ranged from 51% to 114% for naphthalene- d_8 , acenaphthene- d_{10} , phenanthrene- d_{10} , chrysene- d_{12} , and perylene- d_{12} . Concentrations of POP classes were not corrected for recoveries since recoveries were within an established acceptable range.

Statistical analyses were conducted using R (Ver 3.4.1) (R Core Team, 2017). Due to the small sample size, we used geometric mean to estimate the median of samples. A permutation-based Mann–Whitney rank-sum test was employed to ascertain significant differences between two groups using a Monte Carlo simulation to sample all possible permutations. A non-parametric version of ANOVA followed by a Tukey's honestly significant difference test was used to examine the differences between maturity and sex groups. Spearman's rank correlation coefficient was used to analyze potential relationships between

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