Marine Pollution Bulletin 105 (2016) 30–36

Contents lists available at ScienceDirect

Marine Pollution Bulletin

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

Accumulation and temporal changes of PCDD/Fs and dioxin-like PCBs in finless porpoises (*Neophocaena asiaeorientalis*) from Korean coastal waters: Tracking the effectiveness of regulation

Yunsun Jeong [a], Sang-Jo Kim [b], Kyung-Hoon Shin [a], Seung Yong Hwang [c], Yong-Rock An [d], Hyo-Bang Moon [a,*]

[a] Department of Marine Sciences and Convergent Technology, Hanyang University, Ansan 426-791, Republic of Korea
[b] National Fisheries Products Quality Management Service (FiQ), Busan 606-080, Republic of Korea
[c] Department of Bio-Nanotechnology/Molecular and Life Science, Hanyang University, Ansan 426-791, Republic of Korea
[d] Cetacean Research Institute (CRI), National Institute of Fisheries Science (NIFS), Ulsan 680-050, Republic of Korea

ARTICLE INFO

Article history:
Received 12 January 2016
Received in revised form 4 March 2016
Accepted 4 March 2016
Available online 10 March 2016

Keywords:
PCDD/Fs
TEQs
Stockholm Convention
Marine mammal
Temporal trend

ABSTRACT

Temporal trend studies are useful to evaluate the effectiveness of regulations on local pollutants. The emission of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (PCBs) has been regulated by the Korean government in accordance with the Stockholm Convention. The accumulation and temporal trends of PCDD/Fs and dioxin-like PCBs were investigated in finless porpoises (*Neophocaena asiaeorientalis*) collected in Korean waters. Median concentrations of PCDDs, PCDFs, non-*ortho* PCBs, and mono-*ortho* PCBs were 1.0, 1.1, 0.1, and 1.8 pg TEQ/g lipid weight, respectively, which were lower than threshold values for marine mammals. Age- and sex-dependent accumulation patterns were found for PCDFs and DL-PCBs. Temporal trends in finless porpoises collected between 2003 and 2010 showed significant reduction rates of 57%, 54%, 69%, and 60% for PCDDs, PCDFs, non-*ortho* PCBs, and mono-*ortho* PCBs, respectively. Our results suggest that the regulations on dioxin-like contaminants have been effective for marine mammals in Korea.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins, dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) are ubiquitous environmental contaminants (Wania and Mackay, 1996). PCDD/Fs and PCBs have received considerable attentions due to their strong ecotoxicological side effects including reproductive failure, immunotoxicity, and endocrine disrupting effects (Iwata et al., 2004; Schecter et al., 2006). PCDD/Fs and PCBs have been categorized as persistent organic pollutants (POPs) by the Stockholm Convention since 2001 (Fielder et al., 2013).

PCDD/Fs and PCBs are mainly introduced into the environment by waste incineration and chemical manufacturing processes (Olie et al., 1977; Kannan et al., 1998; Domingo et al., 2000). Moreover, PCBs have been intentionally produced and consumed in industrial applications such as oils for transformers and capacitors, and plasticizers (Alcock et al., 1999; Dorneles et al., 2013). In Korea, the nationwide inventory survey for PCDD/Fs reported that the primary sources of PCDD/Fs in the atmosphere are combustion processes from municipal solid waste incinerators (MSWIs) and the steel industry, which collectively accounted for 95% of the total PCDD/F emissions (Moon et al., 2008a, 2008b; Ministry of Environment, 2014). The Korean government (Ministry of Environment) has established an emission standard (0.1 ng TEQ/m^3) of PCDD/Fs in flue gas from MSWIs and has monitored the atmospheric quality of PCDD/Fs since 1997 (Ministry of Environment, 2010; Kim and Yoon, 2014). The total emissions of toxic equivalents (TEQs) of PCDD/Fs generated from waste incinerators in 2001 were reduced by 88% in the past 10 years (Ministry of Environment, 2014).

Marine mammals are top-level predators in the marine ecosystem and contain high levels of POPs in their fat tissues. Because of their long life spans and the lower metabolic capacity of toxic organic contaminants, marine mammals have been utilized as bioindicators of contamination by POPs including PCDD/Fs and DL-PCBs (Moon et al., 2010a, 2010c; Vorkamp et al., 2011). According to a report by the Cetacean Research Institute (CRI) in Korea, approximately 12 cetacean species inhabit the coastal waters of Korea (An and Kim, 2008). Representative species are finless porpoises (*Neophocaena asiaeorientalis*), common dolphins (*Delphinus capensis*), and minke whales (*Balaenoptera acutorostrata*), which accounted for about 80% of total by-caught species in Korea (Moon et al., 2010a, 2010b). Finless porpoises (*N. asiaeorientalis*) are frequently by-caught by fisherman from the western and southern parts of the coastal waters of Korea due to their smaller body size and larger populations compared to other species (Lee et al., 2013). Previous studies have reported that high accumulations of PCDD/Fs, PCBs, organochlorine pesticides (OCPs), and polybrominated diphenyl ethers (PBDEs) in finless

* Corresponding author.
E-mail address: hbmoon@hanyang.ac.kr (H.-B. Moon).

http://dx.doi.org/10.1016/j.marpolbul.2016.03.007
0025-326X/

porpoises (*N. asiaeorientalis*) from Asian coastal waters are associated with their health status (Ramu et al., 2005; Hung et al., 2006; Moon et al., 2010a; Park et al., 2010; Isobe et al., 2011).

A temporal trend study is an essential tool for assessing the effectiveness of legislative action on target contaminants in the environment (Lam et al., 2009; Rigét et al., 2010). Based on the regulation of the PCDD/Fs in flue gas from MSWIs, the concentrations of PCDD/Fs in the atmosphere have clearly decreased for the last decade (Ministry of Environment, 2014). However, the temporal trends in PCDD/Fs and PCBs are not clear in sediment and bivalves from Korean coastal waters during 2001–2007 (Choi et al., 2010, 2011). To date, only one study has evaluated the temporal trends of PCDD/Fs and DL-PCBs using the aquatic mammal the Baikal seal (*Pusa sibirica*) from Russia (Imaeda et al., 2009). Our previous studies determined that there is considerable accumulation of PCDD/Fs and DL-PCBs in common dolphins (*D. capensis*), minke whales (*B. acutorostrata*), and finless porpoises (*N. asiaeorientalis*), which are comparable to the threshold values for marine mammals (Moon et al., 2010a, 2010b, 2010c). However, no comprehensive studies are available on the temporal trends in PCDD/Fs and DL-PCBs using marine mammals in Korea. In the present study, we assessed the effectiveness of the regulation of PCDD/Fs and DL-PCBs with time-gap finless porpoises (*N. asiaeorientalis*) samples. In addition, we investigated the accumulation status and ecotoxicological implications of PCDD/Fs and DL-PCBs in these species inhabiting Korean coastal waters.

2. Materials and methods

2.1. Sample collection

Blubber samples ($n = 76$) were obtained from finless porpoises entangled in fishing nets along the Yellow Sea (Sinjin Island, Eocheong Island, Oeyeong Island, and Daecheon coast) from March to June 2010 (Fig. 1). By-caught samples were transported to the laboratory of the Cetacean Research Institute (CRI) after biometric measurements such as body length and weight. To investigate the age-dependent accumulation of PCDD/Fs and DL-PCBs in finless porpoises, age was determined by decalcified thin sections of teeth (Lee et al., 2013). Sexual maturity was determined by the presence of corpora for females and the weight of the testes and histological examination for males (Lee et al., 2013). Collected porpoise samples were divided into four groups depending on sex and growth stage: immature male ($n = 19$), immature female ($n = 18$), mature male ($n = 19$), and mature female ($n = 10$). All the samples were stored at −20 °C until analysis.

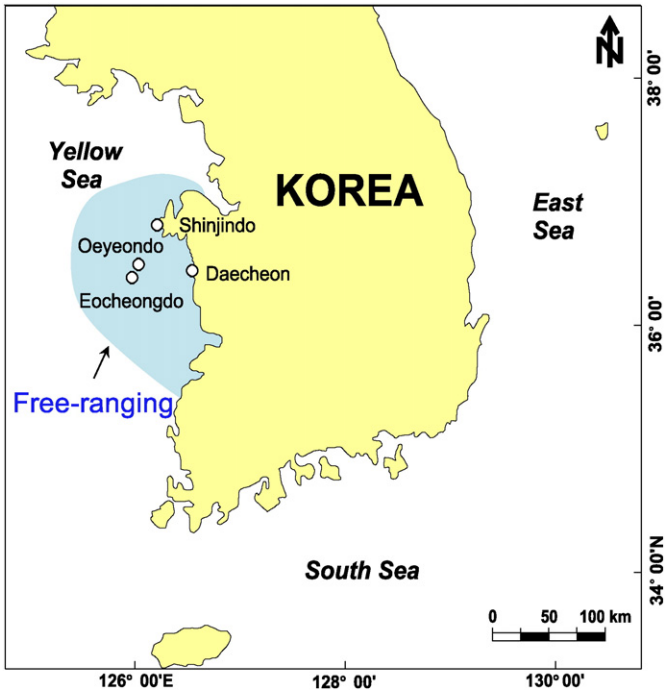

Fig. 1. Sampling map and geographical distribution of the finless porpoises (*Neophocaena asiaeorientalis*) collected from Korean coastal waters in 2010.

2.2. Chemical analysis

Details of the preparation of PCDD/Fs and DL-PCBs in blubbers have been presented elsewhere (Moon et al., 2010a, 2010b). In our study, 17 PCDD/F congeners (2,3,7,8-TCDD/F, 1,2,3,7,8-PeCDD/F, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDD/F, 1,2,3,6,7,8-HxCDD/F, 1,2,3,7,8,9-HxCDD/F, 2,3,4,6,7,8-HeCDF, 1,2,3,4,6,7,8-HpCDD/F, 1,2,3,4,7,8,9-HpCDF, OCDD, and OCDF) and 12 DL-PCB congeners (IUPAC No.: CBs 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189) were analyzed in blubber samples using methods described elsewhere (Moon et al., 2010a, 2010b). In brief, approximately 1 g of blubber samples were homogenized with anhydrous Na_2SO_4 and extracted in mixed solvent of dichloromethane (DCM, ultra-residue analysis, J.T. Baker, Phillipsburg, NJ, USA) and hexane (ultra-residue analysis, J.T. Baker) using a Soxhlet apparatus. Prior to the extraction, CBs 103, 198, and 209, obtained from AccuStandard (New Haven, NJ, USA), were spiked into the samples as surrogate standards. The extract was concentrated to 11 mL, and a 1 mL aliquot was used for the gravimetric determination of lipid content. To remove lipid, the remaining extract (10 mL) was passed through a gel permeation chromatography (GPC) column packed with Bio-beads S-X3 (Bio-Rad Laboratories, Hercules, CA, USA) and a cartridge packed with 0.5 g of silica gel (neutral, 70–230 mesh, GL Sciences, Tokyo, Japan). The extract was divided into two portions of PCDD/Fs (5 mL) and DL-PCBs (4 mL) prior to a clean-up procedure. For determination of PCDD/Fs and DL-PCBs, 13C-labeled PCDD/Fs (EPA-1613LCS; Wellington Laboratories, Guelph, ON, Canada) and 13C-labeled DL-PCBs (WP-LCS; Wellington Laboratories) were spiked into each aliquot as internal standards. The extract for PCDD/F analysis was cleaned by passing it through a multi-layer silica gel column using 200 mL of hexane. The eluants were fractionized on an activated alumina column using successive portions of 3% DCM in hexane and then 50% DCM in hexane. The second fraction was used for determination of PCDD/Fs. The aliquot for DL-PCBs was passed through a multi-layer silica gel column using 15% DCM in hexane.

2.3. Instrumental analysis and quality control

The details of instrumental analysis have been presented elsewhere (Moon et al., 2010a, 2010b). Briefly, the PCDD/F and DL-PCB congeners were measured using high resolution gas chromatography interfaced with high resolution mass spectrometry (HRGC/HRMS; JMS 800D, JEOL, Tokyo, Japan). PCDD/Fs and DL-PCBs were quantified using the isotope dilution method, based on relative response factors (RRF) of individual congeners. The HRMS was operated in electron ionization (EI) mode, and ions were monitored by selected ion monitoring. An SP-2331 gas chromatography column (60 m length, 0.25 mm inner diameter, 0.2 μm film thickness; Supelco, Bellefonte, PA, USA) was used for the separation of tetra- to hexa-CDD/Fs, and DB5-MS (60 m length, 0.25 mm inner diameter, 0.25 μm film thickness; J&W Scientific, Palo Alto, CA, USA) was used for the separation of hepta- and octa-CDD/Fs. DL-PCBs were analyzed using an DB5-MS (30 m length, 0.25 mm inner diameter, 0.25 μm film thickness).

Procedural blanks ($n = 7$) were processed every 10 samples to check for background contamination and did not contain quantifiable amounts of the PCDD/Fs and DL-PCBs. Solvents injected before and after the injection of standards showed negligible carryover. The recovery of surrogate standards (CBs 103, 198, and 209), spiked before the extraction, was 96 ± 31% (average ± standard deviation). Recovery of