Marine Pollution Bulletin 60 (2010) 768–774

Contents lists available at ScienceDirect

Marine Pollution Bulletin

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

Baseline

Edited by Bruce J. Richardson

The objective of BASELINE is to publish short communications on different aspects of pollution of the marine environment. Only those papers which clearly identify the quality of the data will be considered for publication. Contributors to Baseline should refer to 'Baseline—The New Format and Content' (*Mar. Pollut. Bull.* **60**, 1–2).

Organohalogen contaminants in finless porpoises (*Neophocaena phocaenoides*) from Korean coastal waters: Contamination status, maternal transfer and ecotoxicological implications

Bu-Kyeong Park [a,b], Gyum-Joon Park [a], Yong-Rock An [a], Hee-Gu Choi [a], Gi Beum Kim [b], Hyo-Bang Moon [c,*]

[a] *National Fisheries Research and Development Institute (NFRDI), 408-1, Sirang-ri, Gijang-eup, Gijang-gun, Busan 619-705, Republic of Korea*
[b] *Department of Marine Environmental Engineering, Marine Industry Institute, Gyeongsang National University, Tongyeong 650-160, Republic of Korea*
[c] *Department of Environmental Marine Sciences, College of Science and Technology, Hanyang University, Ansan 426-791, Republic of Korea*

ARTICLE INFO

Keywords:
Marine mammals
Organochlorine compounds
Polybrominated diphenyl ethers
Finless porpoises
Debromination

ABSTRACT

Information on the occurrence of organochlorine compounds (OCs) and polybrominated diphenyl ethers (PBDEs) in marine mammals from Korea is scarce. In this study, OCs and PBDEs were determined in the blubber of 52 finless porpoises (*Neophocaena phocaenoides*) from Korean coastal waters. The highest contamination was found for DDTs, followed by PCBs, PBDEs, HCHs, CHLs and HCB. Concentrations of OCs in finless porpoises were lower than those reported worldwide, but PBDE contamination was comparable to other studies, due to ongoing use of PBDE products in Korea. Significant gender-specific differences were found for concentrations and accumulation profiles of OCs and PBDEs, due to maternal transfer and lactation of mature females. The BDEs 49 and 66 comprised 4–16% of total PBDEs in finless porpoises, which seems to be associated with debromination of higher BDEs. The DDT levels in Korean finless porpoises have almost reached the levels associated with immunosuppression in marine mammals.

Contamination by persistent organic pollutants (POPs) is of global concern because they are toxic, persistent and can bioaccumulate in wildlife and humans. Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) are representative compounds of POPs. Organochlorines (OCs), including PCBs and OCPs, have shown decreasing trends in the environment over the past few decades (Ramu et al., 2006; Isobe et al., 2009). However, they are still present in coastal and offshore environments and human tissues in Korea (Kang et al., 2008; Moon et al., 2008, 2009a; Won et al., 2009). Polybrominated diphenyl ethers (PBDEs) are brominated flame retardants (BFRs) used in electronics, plastics, paints, textiles, and building materials (Watanabe and Sakai, 2003). PBDEs have been shown to exert neurodevelopmental and endocrine-disrupting effects in laboratory animals (Birnbaum and Staskal, 2004; Costa and Giordano, 2007). In 2009, the Stockholm Convention included penta- and octa-BDEs in the list of POPs. BFRs are not produced in Korea but are imported from various countries. The major component of BFRs is deca-BDE, which accounts for 25% (12,324 tons) of the total BFR demand in Korea (Moon et al., 2007a). Considering the increasing demand for PBDEs with the rapid growth

* Corresponding author. Tel.: +82 31 400 5534; fax: +82 31 408 6255.
E-mail addresses: hbmoon@hanyang.ac.kr, hbmoon73@hotmail.com (H.-B. Moon).

0025-326X/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.marpolbul.2010.03.023

of the electronics market in Korea, it is important and necessary to investigate the bioaccumulation and ecological risk of PBDEs in marine ecosystems from Korea.

Marine mammals have long life-spans and occupy high trophic levels in aquatic food chains. They have fat reserves in their subcutaneous layers and feed on lipid-rich biota. Therefore, marine mammals have been considered as important species for monitoring POPs contamination and the long-term potential risk in marine ecosystems (Jepson et al., 2005; Hickie et al., 2007; Kannan et al., 2008). In Korea, cetaceans have been traditionally hunted by fishermen for subsistence before the ban on commercial whaling by the moratorium of the International Whaling Commission (IWC) in 1986. However, many cetaceans are still caught as bycatch in fishing nets along the Korean coast. The transport between countries of all cetaceans collected in Korea is restricted because of their inclusion in the Convention of International Trade in Endangered Species of Wild Fauna and Flora (CITES) Appendices I and II (CITES, 1997). Therefore, data on the levels and accumulation profiles of OCs and PBDEs in cetaceans from Korea are scarce (Moon et al., 2009b).

Finless porpoises (*Neophocaena phocaenoides*) are frequently observed cetaceans in the South and Yellow Seas of Korea. Some studies have reported that the accumulation of POPs may have an impact on the health status of finless porpoises in Asian coastal waters (Ramu et al., 2005; Hung et al., 2006). Declining populations of Yangtze finless porpoises in China are associated with a high risk from pollution such as pesticides (Zhao et al., 2008). However, no data are available on the potential health risks of POPs including PBDEs for finless porpoises from Korean coastal waters. The objective of this study was to assess the contamination status, accumulation features and ecotoxicological effects of OCs and PBDEs in finless porpoises from Korea.

Fifty-two blubber samples were collected from finless porpoises entangled in fishing nets along the South and Yellow Seas, Korea May–August 2003 (Fig. 1). Biometric measurements were made and the samples were dissected and transported to a laboratory of the Cetacean Research Institute, Korea. Finless porpoises were divided into four groups, immature male, immature female, mature male, and mature female, based on the sex and the growth stage (Shirakihara et al., 1993). Detailed biological information on the samples is summarized in Table 1. All the samples were stored at −20 °C until extraction.

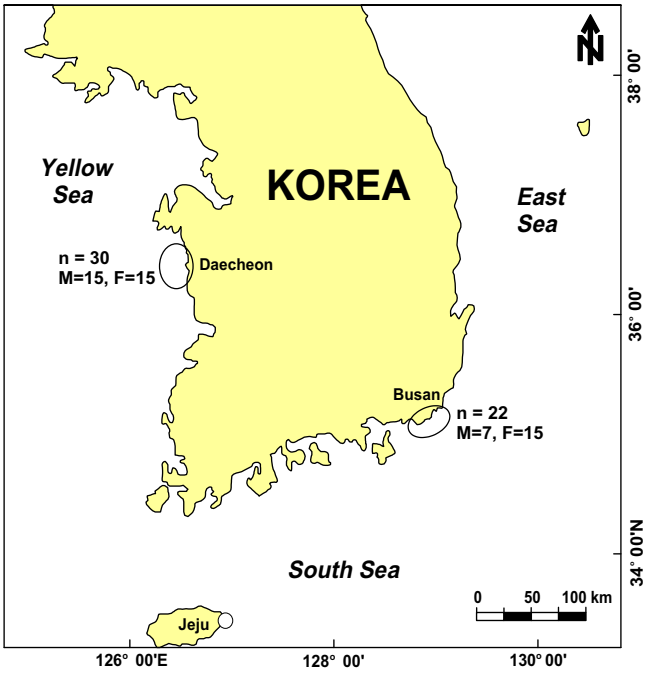

Fig. 1. Sampling map of finless porpoises (*Neophocaena phocaenoides*) from Korean coastal waters.

Concentrations of 22 PCB congeners (PCBs 8, 18, 28, 29, 44, 52, 87, 101, 105, 110, 118, 128, 138, 153, 170, 180, 187, 194, 195, 200, 205 and 206), 23 PBDE congeners (BDEs 17, 28, 47, 49, 66, 71, 85, 99, 100, 119, 126, 138, 153, 154, 156, 183, 184, 191, 196, 197, 206, 207 and 209), and 15 OCP compounds were determined in 52 blubber samples of finless porpoises from Korea. The term DDTs (dichlorodiphenyltrichloroethanes) includes *p,p′*-DDE, *o,p′*-DDE, *p,p′*-DDD, *o,p′*-DDD, *p,p′*-DDT, and *o,p′*-DDT, the term CHLs (chlordanes) includes *oxy*-chlordane, *trans*-chlordane, *cis*-chlordane, *trans*-nonachlor, and *cis*-nonachlor, and the term HCHs (hexachlorocyclohexanes) includes α-, β- and γ-HCH. Hexachlorobenzene (HCB) was included as a target OCP. Internal standards of ^{13}C-labeled PCBs (PCBs 28, 52, 101, 138, 153, 180 and 209) and ^{13}C-labeled PBDEs (BDEs 28, 47, 99, 153, 154, 183, 197, 207 and 209) were purchased from Wellington Laboratories (Guelph, ON, Canada). All solvents were ultra-trace residue analysis grade (J.T. Baker, Phillipsburg, NJ, USA).

Analyses of OCs and PBDEs in blubber samples were performed following methods described elsewhere (Kannan et al., 2008; Moon et al., 2009a). In brief, samples were homogenized with anhydrous Na_2SO_4 and extracted for 20 h in 400 mL of a 3:1 mixture of dichloromethane (DCM) and hexane using a Soxhlet apparatus. Prior to extraction, surrogate standards PCBs 103, 198 and 209 were spiked into the samples. An aliquot of extracted samples was sub-sampled for lipid measurement. Lipids were removed from the extracts by gel permeation chromatography using Biobeads S-X3 (Bio-Rad Laboratories, Hercules, CA, USA). The column was eluted with a mixture of 50% DCM in hexane (flow rate 5 mL/min). The first 100 mL of eluate was discarded and the following 150 mL fraction, which contained OCs and PBDEs, was collected and passed through a cartridge packed with 0.5 g of silica gel (neutral, 70–230 mesh, GL Sciences, Tokyo, Japan). The eluant was concentrated to 10 mL and spiked with internal standards, ^{13}C-labeled PCBs and ^{13}C-labeled PBDEs. The extracts were cleaned by passage through a multi-layer silica gel cartridge column with 150 mL of 15% DCM in hexane by Dioxin Cleanup System (DAC695/DPU8; GL Sciences). The eluants were concentrated to approximately 1 mL, and were then evaporated at room temperature to 50–100 μL. The residues were dissolved with 100 μL *n*-nonane for instrumental analysis.

A gas chromatography (Agilent 6980N) coupled to a mass spectrometer (JMS GC Mate II, Jeol, Tokyo, Japan) was used to quantify the PCBs and OCPs. The GC/MSD was operated in the electron impact (70 eV) and selected ion monitoring mode using molecular ions of individual compounds. A DB5-MS capillary column (30 m length, 0.25 mm inner diameter, 0.25 μm film thickness; J&W Scientific, Palo Alto, CA, USA) was used for analysis of PCBs and OCPs. Quantification of each compound was performed by the external standard method. PBDEs were quantified using a high-resolution gas chromatography/mass spectrometer (JMS 800D, Jeol). Analyses were based on the relative response factors of individual congeners. The HRMS was operated in the electron ionization mode, and ions were monitored by selected ion monitoring. PBDE congeners were quantified separately for tri- to hepta-BDEs and octa- to deca-BDEs using a DB5-MS capillary column (15 m length, 0.25 mm inner diameter, 0.1 μm film thickness; J&W Scientific).

Procedural blanks (n = 6) were processed in the same way as the samples and included after every ninth sample. With the exception of the presence of deca-BDE (approximately 1 ng/g) in the blanks, they did not contain quantifiable amounts of the target compounds. The recoveries of PCBs 103, 198 and 209, spiked prior to extraction, ranged from 80 ± 12% (average ± standard deviation). Recoveries of the ^{13}C-labeled PCBs and PBDEs were 93 ± 17% and