### GLOBAL POLLUTION MONITORING OF PCBS AND ORGANOCHLORINE PESTICIDES USING SKIPJACK TUNA AS A BIOINDICATOR

D. Ueno<sup>1</sup>, S. Takahashi<sup>1</sup>, A. N. Subramanian<sup>2</sup>, G. Fillamann<sup>3</sup>, H. Nakata<sup>4</sup>, P. K. S. Lam<sup>5</sup>, J. Zheng<sup>5</sup>, M. Muchtar<sup>6</sup> and S. Tanabe<sup>1</sup>\*

- <sup>1</sup>Center for Marine Environmental Studies (CMES), Ehime University, Tarumi 3-5-7, Matsuyama 790-8566, Japan
- <sup>2</sup>Center of Advanced Studies in Marine Biology, Annamalai University, Parangipettai 608502, Tamil Nadu, India
- <sup>3</sup>Fundação Universidade Federal do Rio Grande, C.P. 474, Rio Grande, RS, 96201-900, Brazil
- <sup>4</sup>Department of Environmental Science, Graduate School of Science and Technology, Kumamoto University, 2-39-1, Kurokami, Kumamoto, Japan
- <sup>5</sup>Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong
- <sup>6</sup>Research and Development Center for Oceanology- Indonesian Institute of Sciences, Jl. pasir Putih 1, Ancol Timur, Jakarta-11048, Indonesia

#### Introduction

Organochlorines (OCs) representing "Persistent Organic Pollutants (POPs)" are well known to have less biodegradable and mobile nature in the abiotic and biotic environment (1). It has been emphasized that oceans play a role as a final sink for persistent toxic contaminants (2) and therefore very slow temporal trend of OCs was reported in the study of marine mammal pollution (3). A large number of monitoring has been done using marine organisms such as mussel to asses the coastal pollution. Whereas only few studies were reported the contamination status of offshore waters using organisms, those information are still fragmental and limited. In order to find the suitable organisms for monitoring the contamination status of POPs OCs in offshore waters, the present study attempted to use skipjack tuna (Katsuwonus pelamis) as bioindicator. Skipjack tuna principally distributes from offshore waters to open seas in tropical and temperate regions almost all over the world such as the Pacific Atlantic and the Indian Oceans (9). This species is an important commercial fish and its ecology and biology has been well studied (8, 9). Such characteristics of skipjack tuna seems to have benefits for monitoring OCs pollution in the open seas. The objectives of this study are to assess the spatial distribution of OCs in offshore waters and open seas, and to elucidate the suitability of skipjack tuna as bioindicator for monitoring OCs.

#### **Materials and Methods**

Skipjack tuna (Katsuwonus pelamis) were collected from offshore waters of various Asian countries (off-Japan, Japan Sea, off-Taiwan, the East China Sea, the South China Sea, off-Philippines, off-Indonesia, the Bay of Bengal), off-Seychelle, off-Brazil and open sea (the North Pacific) during 1996~2001. Some of skipjack tuna were obtained from fish market and fisherman village with confirming the fishing areas. Skipjack tuna from North Pacific were caught by a fishing during a cruse of research vessels.

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Figure 1. Geographical distribution of organochlorine concentrations in skipjack tuna collected from offshore waters of various Asian countries, off-Seychelle, off-Brazil and open seas

Organochlorines, such as polychlorinated biphenyls (PCBs) congeners, DDT and its metabolites (DDTs: p,p'-DDT, p,p'-DDD and p,p'-DDE), chlordane related compounds (CHLs: trans-chlordane, cis-chlordane, trans-nonachlor, cis-nonachlor and oxychlordane), hexachlorocyclohexanes (HCHs:  $\alpha$ -HCH,  $\beta$ -HCH and  $\gamma$ -HCH) and hexachlorobenzene (HCB) were analyzed following the method described in previous study (10, 11).

Chemical analysis of polychlorinated biphenyls (PCBs) congeners followed the methods of Wakimoto *et al.*, (1971). An aliquot of the extract was refluxed with 250 ml of 1 N KOH-ethanol solution for 1 h. PCBs in the extract were transferred to 100 ml of hexane and 250ml of water in a separatory funnel. Hexane layer was concentrated and passed through activated silica-gel (Wako-gel S-1: Wako Pure Chemical Industries Ltd., Osaka, Japan) packed in a glass column. PCBs were eluted with 200ml hexane. After concentration, it was cleaned up with sulfuric acid and then washed with water. Identification and quantification of PCB congeners was performed using a HRGC-MSD (Hewlett-Packard, DE, 6890 series GC coupled with 5973 mass selective detector) having an electron impact (EI). For the quantification of PCBs, an equivalent mixture of Kanechlor 300, 400, 500 and 600 was used as a standard. Total PCB concentration was calculated by adding the concentrations of individual resolved peaks. Peak identification (101 peaks of PCB including major congeners and isomers) was reported previously (Tanabe *et al.*, 1987).

The recoveries in this analytical procedure were  $90.6\pm8.6$  % for insecticides (average of all OC pesticide described above) and  $114\pm3.3$ % for total PCBs (*n*=4). Quality assurance for the measurement of OCs in our present technique was confirmed by analyzing Standard Reference Materials 1945 (Organics in Whale Blubber) provided from The National Institute of Standards and Technology (NIST), and the results agreed well with the NIST certified values. Concentrations of OCs were not corrected for the recoveries and were reported as nanograms per gram on a lipid weight basis.

### **Results and Discussion**

Concentrations of OCs in skipjack tuna from Asian offshore waters, off-Seychelle, off-Brazil and open seas are shown in Fig. 1. PCBs, DDTs, CHLs, HCHs and HCB were detected in all the skipjack tuna analyzed. Among the OCs analyzed in this study, PCBs and DDTs (up to 1800 and 1000 ng/g lipid wt, respectively) were the highest, and those of other OCs were approximately in the order of CHLs > HCHs > HCB (Fig. 1). Residue levels of PCBs, DDTs, CHLs and HCHs in skipjack tuna from the southern hemisphere such as off-Indonesia, off-Seychelle and off-Brazil were apparently lower than those from the northern hemisphere. Such a tendency has also been reported in plants (12) and marine mammals (5, 6). These observations are likely due to larger usage of these compounds in the northern hemisphere.

High concentrations of DDTs and HCHs were observed in skipjack tuna from the East China Sea, the South China Sea and the Bay of Bengal (upto 1300 and 22 ng/g lipid wt, respectively). These results imply that recent usage of technical DDT and HCH for agricultural / public health purposes in China and India. On the other hand, concentrations of PCBs and CHLs were higher in skipjack tuna from off-Japan (upto 1100 and 250 ng/g lipid wt, respectively), implying that pollution sources of PCBs and CHLs still exist in Japanese coastal waters. In general, distribution patterns of PCBs, DDTs, CHLs, HCHs and HCB concentrations found in skipjack tuna were similar to those reported in surface seawaters (13), mussels (4), fishes (14), squids (7), and marine mammals (6) from Asia-Pacific regions. These results suggest that skipjack tuna is a suitable bioindicator for monitoring the global distribution of OCs pollution in offshore waters and open seas.

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