Dioxins and Organohalogen Contaminants in the Far East

Shinsuke Tanabe[1]

[1]Center for Marine Environmental Studies (CMES), Ehime University

The environmental fate and the toxic implications of the thousands of highly persistent toxic substances (PTS) such as *p,p*'-dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexane (HCH), chlordanes (CHL), hexachlorobenzene (HCB), polychlorinated biphenyls (PCBs), polybromiateddiphenyl ethers (PBDEs), polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) etc. are highly complicated. Most of them enter the environment through usage in agriculture, disease control and industries. Some of these are unintentionally produced in the environment and/or byproducts during the manufacturing processes of some other chemicals. These chemicals were found to be lipophilic and bioaccumulative in different tissues and organs of animals and were also presumed to have carcinogenic, terratogenic and endocrine disrupting characteristics (Tanabe, 2002). While many of these chemicals were either banned or under restricted use in most of the developed nations, some developing countries are still using them, thus making the study on their global distribution in the seas and oceans, highly imperative.

Under the umbrella of the Asia Pacific Mussel Watch Program and the Center of Excellence (COE) Program of our Center, we carried out monitoring and toxic evaluation studies of these persistent substances on animals belonging to different trophic levels in the terrestrial and aquatic environments of the Asia Pacific region**.** Since large numbers of evaluation studies are already available from the developed nations in this area we focused our efforts on many of the developing nations such as Cambodia, China, Vietnam, India, Indonesia, Malaysia, Russia, and Philippines as well as the developed nations like Korea and Japan.

Our studies on the distribution of organochlorines in this region using the green mussels (*Pernaviridis*) showed that PCBs pollution is higher mainly in Japan, Russia and Philippines, DDTs came from China, Hong Kong and Vietnam and HCHs has been mainly contributed by India, China and Russia. Further the studies carried out on the fish, skipjack tuna (*Katsuwonuspelamis*) in this region showed that the pollution by these chemicals in the biota strictly follow their transport characteristics, rather than their usage pattern in the nearby land areas. HCHs even though it has been widely used in the tropical countries, were more in the fish from northern waters plausibly because of their higher transportability (Fig. 1). DDTs with high octanol-water coefficient and low transportability were higher in tropical and subtropical individuals. Higher PCBs and CHLs were found in skipjack tuna from mid-latitudes**.** The higher trophic animals, the cetaceans, demonstrated a same type of latitudinal distribution of these chemicals, obviously through food chain accumulation. Dioxin like compounds showed apparently higher concentrations in albatrosses collected from North Pacific than from Southern Ocean, indicating larger emission sources in Northern hemisphere than Southern Hemisphere.

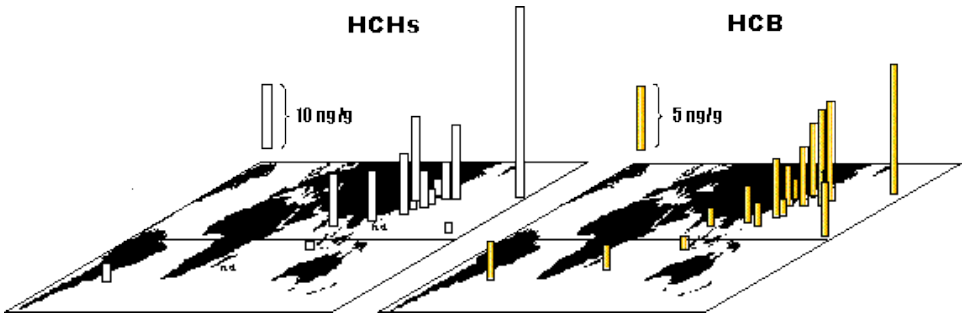

Fig. 1. Geographical distribution of HCHs and HCB in skipjack tuna collected from Asia Pacific region

Our recent findings have indicated the presence of another class of halogenated contaminants, namely polybromianteddiphenyl ethers (PBDEs), structurally and characteristically similar to the classic organochlorines like PCBs and DDTs in skipjack tuna and also in the cetaceans of this area. The results showed that the levels in the

specimens from East China Sea were apparently higher than in developed nations like Japan and Korea indicating that developing Asian nations also have some sources for this industrial chemical, which is also substantiated by the usage statistics of these chemicals in different nations (Ueno et al., 2004;Kajiwara et al., in press) Further these compounds are widely present in the human breast milk from several Asian countries such as Japan, China, Malaysia, Korea, Philippines, Cambodia, Vietnam and India **(Fig. 2)** indicating a widespread pollution by PBDEs in the Asia Pacific region. Unlike the organochlorine compounds in human milk, there was no significant difference (p>0.05) on PBDEs concentration between locations, indicating no ubiquitous sources controlling the regional PBDEs levels.

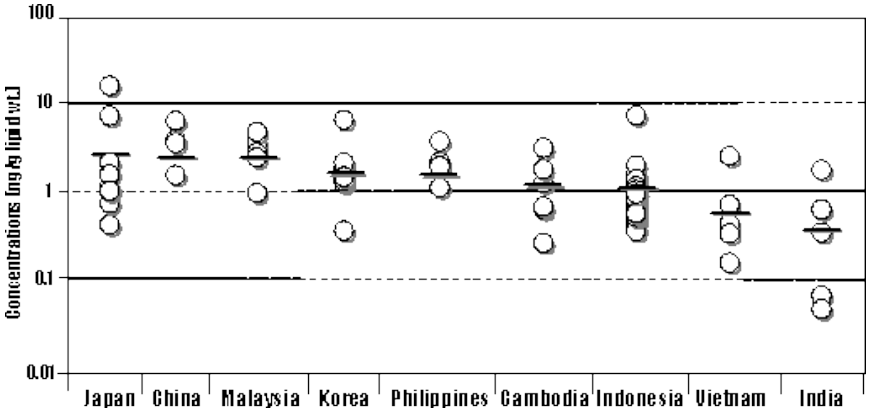

Fig. 2. Concentrations of PBDEs in Asian human breast milk

Temporal trends of PBDEs in marine mammals of our studies and elsewhere showed an increasing trend from the 1970s to the mid-1990s followed by a decreasing trend after the late 1990s. The congener profiles of PBDEs in the archived samples of northern fur seals also indicated such changing patterns of different congeners with time. While some of the Stockholm Convention designated POPs in northern fur seals were the highest in the 1970s to early 1980s and then decreased, PBDEs were lower in the 1970s but much higher in the 1990s. Further, the PBDEs levels in the Japanese specimens of melon-headed whales and the finless porpoises from Chinese coastal waters were much higher in the recent specimens than those a decade before. All our above studies validates the need for continued long-term monitoring of POPs even after their ban and also the necessity of addition of compounds like PBDEs to the already existing list of POPs.

Our studies also revealed an important matter of concern that the wide open municipal dumping sites in many developing countries are also becoming major sources of the highly toxic compounds like polychlorinated dibenzo dioxins (PCDDs) and polychlorinated dibenzo furans (PCDFs). Soils in those dump sites were found to have these chemicals at considerable concentrations. As a result, higher levels of dioxins and related compounds were found to exist in the human breast milk samples from the mothers living near such dump sites in the Philippines, Cambodia, Vietnam and India **(**Kunisue et al., 2004). Higher dioxin levels were found to affect the Vitamin A concentrations in those mothers. Unlike in the case of other classical organochlorines which normally accumulate in the lipid rich tissues of the animals, dioxins and furans were found to accumulate preferentially in the liver of the organisms as revealed by the liver adipose tissue ratios of different organisms in our study (**Fig. 3**).

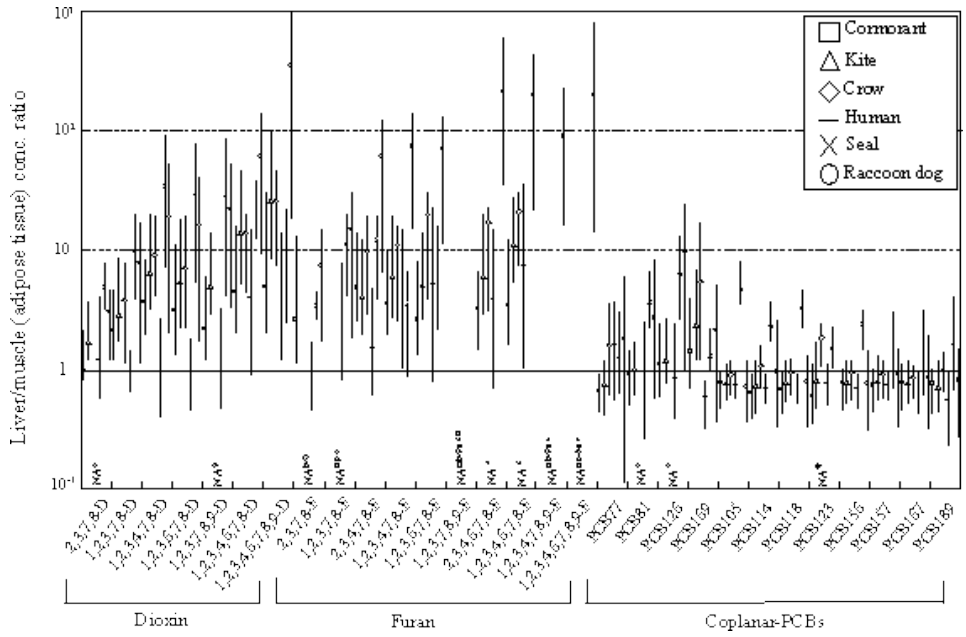

Fig. 3. Liver/adipose tissue ratios of dioxins and related compounds in Wildlife and human

Elucidation of toxic potential of all these organohalogen compounds on a variety of animals showed that marine mammals have a comparatively low capacity to decompose these contaminants and retain them to higher levels in their bodies, which may lead to high toxic risk of exposure. Additionally, physiological dysfunctions such as abortion, sterility, mass mortality, tumors, etc., by exposure to these toxic contaminants have also been suggested in cetaceans and pinnipeds, based on CYP enzyme and hormonal studies (Iwata et al., 2004). Further, the temporal trend evaluations of these chemicals, carried out on the archived samples of Baikal seals, Caspian seals and minke whales, showed that the recent contamination by organochlorines in waters near to source areas considerably decreased when compared with their severe pollution in the 1970s, but pollution in remote oceans still continues without any apparent decline, indicating the need for long-term monitoring even after the ban of a particular chemical.

Iwata, H., M. Watanabe, Y. Okajima, S. Tanabe, M. Amano, N. Miyazaki and E.A. Petrov, 2004.Toxicokinetics of PCDD, PCDF, and coplanar PCB congeners in Baikal seals, Pusasibirica: age related accumulation, maternal transfer, and hepatic sequestration. Environ. Sci. Toxciol., 38: 3505-3513.

Kajiwara, N., S. Kamikawa, K. Ramu, D. Ueno, T. Yamada, A. Subramanian, P.K.S. Lam, T.A. Jefferson, M. Prudente, K. Chung and S. Tanabe, (in press). Geographical distribution of polybromianteddiphenyl ethers and organochlorines in cetaceans from Asian waters. In: Spl. Issue of Chemosphere on BFRs in the Environment. MehranAlaee (Ed.).pp.

Kunisue, T., M. Watanabe, H. Iwata, A. Subramanian, I. Monirith, T.B. Minh, R. Baburajendran, T.S. Tana, P.H. Viet, M. Prudente and S. Tanabe, 2004. Dioxins and related compounds in human breast milk collected around open dumping sites in Asian developing countries: Bovine milk as a potential source. Arch. Environ. Contam.Toxicol., 47 : 414-426.

Tanabe,S. 2002: Contamination and toxic effects of persistent endocrine disrupters marine mammals and birds. Marine Pollution Bulletin, 45: 69-77.

Ueno, D., N. Kajiwara, H. Tanaka, AN. Subramanian, G. Fillmann, P.K.S. Lam, G.J. Zheng, M. Muchitar, H. Razak, M. Prudente. K. Chung and S. Tanabe, 2004. Global pollution monitoring of polybrominateddiphenyl ethers using skipjack tuna as a bioindicator. Environ. Sci. Technol., 38 : 2312-2316.