Dioxin '97, Indianapolis, Indiana, USA

OCCURRENCE AND BEHAVIOR OF EXTRACTABLE ORGANIC HALOGEN (EOX) AND MAN-MADE ORGANOCHLORINES IN HARBOR PORPOISE (*Phocoena phocoena*) FROM THE POLISH COAST OF BALTIC SEA

M. Kawano[1], J. Falandysz[2], Y. Tanaka[1] and T. Wakimoto[1].

1: Department of Environment Conservation, Ehime University
Tarumi 3-5-7, Matsuyama 790, Japan
2: Department of Environmental Chemistry and Ecotoxicology, University of Gdañsk
ul. Sobieskiego 18, PL 80-952, Gdañsk, Poland

Introduction

It is evident that large amounts and many kinds of man-made substances are introduced to the environment. Many studies have been performed to make clear the distribution of man-made chemicals like organochlorine compounds[1]. It is known that these synthetic organochlorine compounds are accumulated extensively in higher trophic organisms such as marine mammals[2]. However, complete data of extractable organic halogen (EOX) and other organochlorines are yet to be detected and quantified. It may be true that there are methodological problems with current measurements for complicated residues in these mammals. Instrumental neutron activation analysis is a suitable technique for organic halogen residued in environmental samples[3]. Analysis of EOX will be of help to understand the levels of unidentified organic halogens when EOX and identified man-made organic halogen concentrations are compared[4].

The Baltic Sea is a one of the heavily polluted sea. Considerable concern about contamination of the Baltic Sea has been generated by suspected leakage of hazardous waste dumps and by many chemical outfalls along the Scandinavian and Easter European countries including Russia[5]. The objective of the present study is to determine the concentrations of EOX and to investigate their accumulation properties in harbor porpoise from the Baltic Sea.

Materials and Methods

Eight individuals of Harbor porpoise (*Phocoena phocoena*) and four individuals of herring (*Clupea harengus*) from the Baltic Sea were used for this study. These organisms were collected during 1989 to 1995. The blubber samples of marine mammals and whole body of fish samples were extracted using a homogenizer. Using organic solvent technique, EOX was extracted from above mentioned samples. Further, the extract was washed with distilled and deionized water, and fractionated with S-X3 (Bio-Lad Laboratories Inc.) gel permeation column chromatography[6].

Finally, extract sample was sealed in a polyethylene vial and covered with a polyethylene bag on surface. Activation technique was carried out by using neutron flux at a rate of 3.7×10^{13} n/cm^2-sec for two minutes using a research reactor (JRR-4). This experiment was conducted at Japan Atomic Energy Research Institute (JAERI), Ibaragi, Japan. The gamma-rays from ^{38}Cl, ^{80}Br and ^{128}I were measured by gamma-ray spectrometry technique[7]. The reproducibility of this method is 11 % for chlorine, 5.0 % for bromine and 13 % for iodine (n=3). Individual organochlorine compounds like PCBs, DDTs, HCHs and chlordanes (CHLs) were analysed by GC-MS and GC-ECD[2]. The analytical error of this method was less than 5 %.

Results and Discussion

Analytical results of EOX are shown in Table 1. Table 1 summarizes data on EOX in a few species of marine mammals from Pacific Ocean[4]. EOX in the blubber samples of harbor porpoise ranged from 23 to 50 mg kg^{-1}. EOX concentrations in the samples from mid-Pacific region are relatively higher than those in the organisms from the Baltic Sea. It is known that mid-latitude in the Northern Hemisphere is heavily polluted by chemicals which are originated from industrial activities. Because, developed countries are located on mid-latitude. It is estimated that exposure time is another factor for the residue levels of EOX.

The order of concentrations in these samples was extractable organic chlorine (EOCl) > extractable organic bromine (EOBr) > extractable organic iodine (EOI) (Fig. 1). It appears that percent composition of EOCl in EOX is relatively high in the samples from the Baltic Sea. Among marine mammals, the lowest composition percent of EOCl in EOX was found in the blubber samples of striped dolphin. It is known that many pulp and paper industries are located on the coastal area of the Baltic Sea[8]. Accordingly, many chemicals are produced in processes of bleaching. It can be considered that large amounts and many kinds of hydrophobic halogenated-compounds have been produced in paper mill industry located along with the coast of Baltic Sea and discharged to the sea as bleached-kraft mill effluents.

It is well known that man-made organochlorine compounds are distributed over the globe. These compounds are stable in the environment and are accumulated in wildlife[2]. Especially, DDTs, PCBs, HCHs and CHLs are known as main contaminants in the environment. Accordingly, the concentrations of these compounds were analysed and organic chlorine contained in these compounds were calculated as known EOCl in order to compare with the figures of EOX. The concentration of known EOCl is substracted from the total organic chlorine (EOCl) to give the concentration of unknown EOCl (Fig.2). Fig.2 shows percent compositions of known EOCl, unknown EOCl, EOBr and EOI. This figure clearly shows that the percent composition of unknown EOCl fraction in EOX determined in harbor porpoise is the highest among the samples analysed. This result suggests that the organism in the Baltic Sea is relatively contaminated by unknown organic chlorine compounds.

It is known that inert compounds which resist metabolism in organisms accumulate through food chain. Namely, it is known that accumulation capacities (i.e. bioaccumulation) of compounds or some fraction separated operationally might give information about persistency in organism and through ecosystem. Accordingly, in order to understand bioaccumulation of EOX, the biomagnification factor (BMF) was determined, which is the ratio of EOX concentration in marine mammal (harbor porpoise) to EOX concentration in fish (herring). The result shows that

Table 1. Concentrations (μg/g on wet weight basis) of EOX in Cetaceans.

Species	n	EOCl	EOBr	EOI
Baltic Sea				
Harbor Porpoise (*Phocoena phocoena*)	8	36 (22-48)	1.7 (0.57-2.2)	0.69 (0.18-1.4)
Pacific Ocean				
Striped Dolphin* (*Stenella coeruleoalba*)	15	110 (47-120)	46 (31-54)	5.8 (3.8-7.6)
Dall's Porpoise* (*Phocoenoides dalli*)	6	25 (33-57)	5.9 (5.5-19)	1.9 (1.6-4.3)

* Data from Kawano et al[4].
Figures in brackets indicate concentrations on fat weight basis.

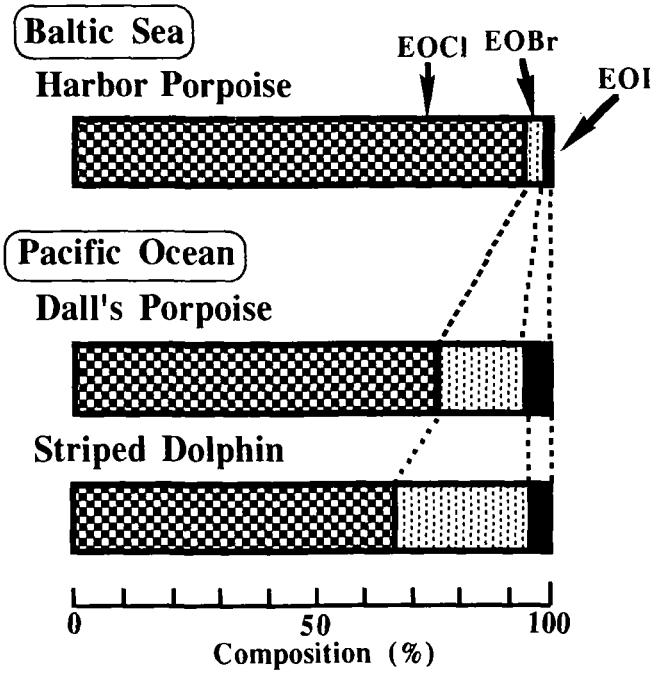

Fig.1 Composition of EOX (EOCl, EOBr and EOI) in various marine Mammals.

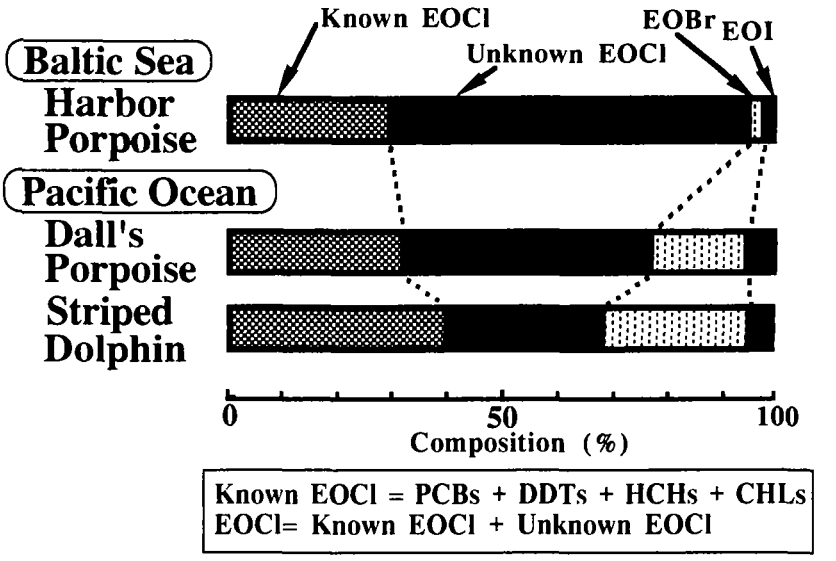

Fig. 2 Composition of EOX and EOCl (known and unknown fractions).

BMF of EOBr is the highest among halogens investigated. It is considered that the constituents in EOBr of harbor porpoise are probably highly persistent in the Baltic marime ecosystem. EOBr was the most persistent fraction in EOX detected in cetacean from Pacific Ocean[9].

Despite the global spread of several man-made organolalogens, primary known industrial pollutants are only responsible for rather small fraction of the EOX present in the Baltic aquatic environment. Some kinds of compounds are produced in marine organisms like algae, sponges and so on[10]. It is necessary to investigate the possibility regarding natural products occurred in the unknown fraction in EOX, also. It is concluded that some constituents in marine organisms are man-made and/or stable natural produsts which might be accumulated through food chain.

Acknowledgments

The authors wish to express their sincere appreciation all those who contributed to this study. This study was supported by a Grant-in Aid from the Ministry of Education, Science and Culture of Japan (Project No.08680554) and by the Polish Committee of Scientific Research (KBN). The neutron activation analysis had been carried out at the Inter-University Laboratory for the Joint Research Using the JAERI Facilities.

References

1) Sladen, W.J.L., Menzie, C.M. and Rechel, W.L., DDT residues in Adelie penguines and a crabeater seal from Antarctic. Nature, 210, 670-673 (1966)

2) Kawano, M., Inoue, T., Wada, T., Hidaka, H. and Tatsukawa, R.: Bioconcentration and residue patterns of chlordane compounds in marine animals: invertebrates, fisf, mammals, and sea birds. Environ. Sci. Technol., 22, 792-797 (1988)

3) Kawano, M. and Tatsukawa, R., Neutron Activation Analysis (NAA) 3. NAA in Environmental Sciences: 1. Total organic halogens in the environment., Radioisotopes, 43, 228-232 (1994) (in japanese)

4) Kawano, M., Yoshioka, H., Tejima, Y. and Tatsukawa, R., Occurrence of organic halogens in marine mammals. pp333-337. in "Naturally-Produced Organohalogens" Edited by Grimvall, A. and De Leer, Ed W. D., Kluwer Academic Publishers, Dordrecht, The Netherlands (1995)

5) Otzen, F., Second Periodic Assessment of the State of the Marine Environment of the Baltic Sea, 1984-1988: Background document, Baltic Marine Environment Protection Commission, Helsinki Commission, Helsinki, 1-69 (1990)

6) Tatsukawa, R., Kawano, M., Hidaka, Y. and Tejima, Y., Extractable organic halogens (Cl, Br and I) in environment, Annual Report of the Inter-University Joint Research Using the Japan Atomic Research Institute Facilities (JAERI), Research Center for Nuclear Science and Technology, University of Tokyo, Tokyo, 49-51 (1990)

7) Kawano, M., Falandysz, J., Tsiji, S., Kitamura, S. and Wakimoto, T., Extractable organic halogen (EOX) and man-made organochlorine compounds in soils and sediments from northern Poland. J. Environ. Chem., 7, 7-13 (1997) (in Japanese)

8) *Wulff, F., Rahm, L., Jonsson, P., Brydsten, L., Ahl, T. and Granmo, A., A mass-balance* model of chlorinated organic matter for the Baltic Sea -A challenge for ecotoxicology, AMBIO, 22, 27-31 (1993)

9) Kawano, M., Tanaka, Y. and Tatsukawa, R., Occurrence of extractable organic halogen (EOX) in some marine organisms, Proceedings on 19th Conference of the Baltic Oceanographers, August, Sopot, Poland, 732-738 (1994)

10) Gribble, G. W.: The natural production of chlorinated compounds. Environ. Sci. Technol., 28, 310A-319A (1994)