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Short Note

Accumulation of organochlorines in the fin whale *Balaenoptera physalus* and the finless porpoise *Neophocaena phocaenoides* from the Ibaraki coast, Japan

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Abstract—Concentrations of persistent organic pollutants (POPs) and HCHs were examined in the muscle of the fin whale, *Balaenoptera physalus* stranded at Kita Wharf of Ibaraki Prefecture, Japan. The compounds were also examined in the muscle, liver, and blubber of the finless porpoise *Neophocaena phocaenoides* bycaught off Ibaraki Prefecture, Japan. The concentrations of POPs in muscle samples in finless porpoise were 2 to 10 times higher than those in fin whale. This might be the result of differences in prey resources. Percentage composition of chlordanes (CHLs), hexachlorocyclohexanes (HCHs), and DDTs were determined in muscle samples. These compounds appeared further degraded in fin whale than in finless porpoise. This result indicates that fin whale might have a higher degradation ability than finless porpoise.

Key words: fin whale, finless porpoise, organochlorine, bioaccumulation

Introduction

Persistent organic pollutants (POPs) are highly undegradable in the environment, accumulate in living organisms, have long range atmospheric transport, and are toxic to humans and wildlife. They were used mainly as pesticides in agriculture beginning in the 1950s. POPs are now banned in most countries, but are still used in some countries as pesticides. Their potential for long range transport and cold condensation (Wania and Mackay 1995, Iwata et al. 1993) lead to global pollution, and POPs are detected even in the polar regions (Weber and Goerke 2003, Goerke et al. 2004). In addition to global pollution, another major concern of POPs is bioaccumulation. Since POPs are lipophilic and have a resistance to metabolization, they accumulate through the food chain (Camfens and Mackay 1997). Therefore POPs accumulate at high levels in marine mammals, which are at the top of the aquatic food chain. This makes marine mammals vulnerable to POPs. Many studies have reported the effects of POPs on marine mammals (e.g., Aguilar and Borrell 1994, Evans et al. 2004), and organochlorines are known to affect the immune system (Tanabe et al. 1984). Also, there are concerns about carcinogenicity, tetratogenicity, and reproductive abnormalities (e.g., Tanabe et al. 1994, Subramanian et al. 1987, Martineau et al. 1994).

In Japan, POPs are still detected in marine organisms (Ueno et al. 2003, Kajiwara et al. 2002), although most POPs were banned in the 1970s. Thus, the objective of the present study was to accumulate basic information on POP levels in two marine mammals, the fin whale *Balaenoptera physalus* and the finless porpoise *Neophocaena phocaenoides* off the Ibaraki coast.

Materials and Methods

Sample collection

The muscle sample from fin whale was collected from a dead animal stranded at Kita wharf of Toukaimura, Japan, on March 16, 2004 (Table 1). The liver, blubber, and muscle samples of finless porpoise were collected from a dead animal bycaught in Ibaraki Prefecture on May 27, 2004 (Table 1). All materials used for sample collection and preparation were washed thoroughly with purified water and finally washed with an organic solvent such as acetone. All samples

Table 1. Sample data for POPs analysis.

Sample	Sampling date	Sex	Body length (m)	Body weight (kg)
Balaenoptera physalus	2004 March 16	Female	12.5	15000
Neophocaena phocaenoides	2004 May 27	Female	1.04	22.3

were dissected, wrapped in plastic bags, and stored frozen at −20°C until chemical analysis.

Analytical procedure

POP compounds in marine mammals were analyzed following the Monitoring Research Manual (Ministry of the Environment, Government of Japan 2003) with some modification.

About 3 g of homogenized samples were added to a 45 ml Dionex accelerated solvent extraction (ASE Dionex) cell. ^{13}C-labeled surrogate standards were added to the ASE cell. The sample was extracted with a mixture of hexane and acetone (1 : 1) (100°C, static 5 min, heating 5 min, purge 1 min, 2000 psi). The lipid content for each sample was determined gravimetrically. After concentrating the extract, lipids were removed by gel permeation chromatography using teflon column (22–25 mm bore diameter, length 50–70 cm) filled with 50 g resin (BioBeads S-X3) suspended with dichloromethane. The column was eluted with dichloromethane and cyclohexane (1 : 1) at a flow rate of 5 ml/min. The eluent was reduced in volume to about 5 ml. The polar compounds were removed and separated by liquid chromatography on Florisil®. The first fraction, eluted with 100 ml of 5% diethylether in hexane, contained most of the compounds. The second fraction, eluted with 100 ml of 20% diethylether, contained endrin and dieldrin. After reducing to about 5 ml, the first fraction was transferred to silica gel column and separated again into two fractions. The first fraction, eluted with 30 ml hexane, contained HCB and aldrin. The second fraction, eluted with 25% diethylether in hexane, contained the other POPs. All the fractions were reduced in volume to 0.5 ml by dry nitrogen. Syringe spike was added.

An Agilent 6890 series gas chromatography/negative chemical ionization mass spectrometer (Agilent 5973 N) was used for identification and quantification. The separation was carried out with a HT-8 capillary column (SGE, 50 m length×0.22 mm i.d., 0.25 μm film thickness) coated with 8% phenylpolycarborane-siloxane. The column temperature was programmed from 50°C held for 0.3 min, and then increased to 200°C at a rate of 20°C/min. It was further increased to a final temperature of 280°C at a rate of 2.5°C/min. The injector temperature and the ion source temperature were 260°C and 150°C, respectively. Splitless injection (1 μl) of the sample was employed.

All the congeners were quantified using the isotope dilution method to the corresponding 13C-labeled congeners.

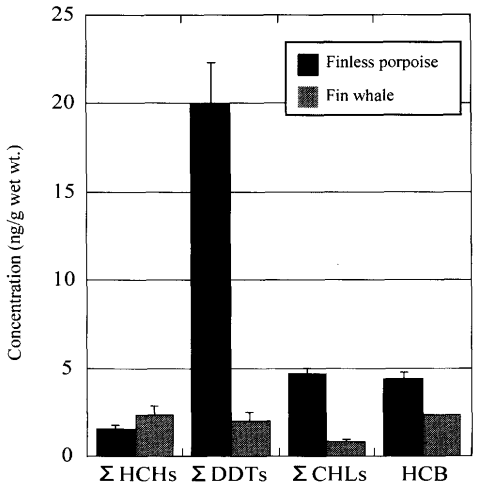

Fig. 1. Concentrations of POPs in muscle of finless porpoise and fin whale.
ΣHCHs = α-HCH + β-HCH + γ-HCH
ΣDDTs = *p,p'*-DDT + *p,p'*-DDD + *p,p'*-DDE + *o,p'*-DDT + *o,p'*-DDD + *o,p'*-DDE
ΣCHLs = *trans*-chlordane + *cis*-chlordane + *cis*-nonachlor + *trans*-nonachlor + oxychlordane

The recovery for each sample was between 50–120%. The detection limit of each compound was in the range of 0.13–5.00 pg g^{-1}.

Results and Discussion

Concentrations of POPs in muscle samples of the fin whale and finless porpoise from the Ibaraki coast

POP levels in muscle samples of finless porpoise and fin whale are shown in Fig. 1. The concentrations of ΣDDTs, ΣHCHs, ΣCHLs, and HCB in finless porpoise were 20.05, 1.56, 4.65, and 4.41 ng g^{-1} wet wt., respectively, and 1.99, 2.32, 0.77, and 2.32 ng g^{-1} wet wt., respectively, in fin whale. ΣDDTs was predominant in the sample from the finless porpoise, and the other compounds were found at much lower concentrations. Finless porpoise had higher level of POPs (2 to 10 times) than fin whale for all compounds except ΣHCHs. Finless porpoise are known to feed on cephalopods and fish (Shirakihara et al. 1992). On the other hand, fin whales feed mostly on euphasiids and copepods (Flinn et al. 2002). The cephalopods and fish are at higher levels in the food chain than the euphasiids and copepods. Thus, the difference in diet may have resulted in the difference in POP

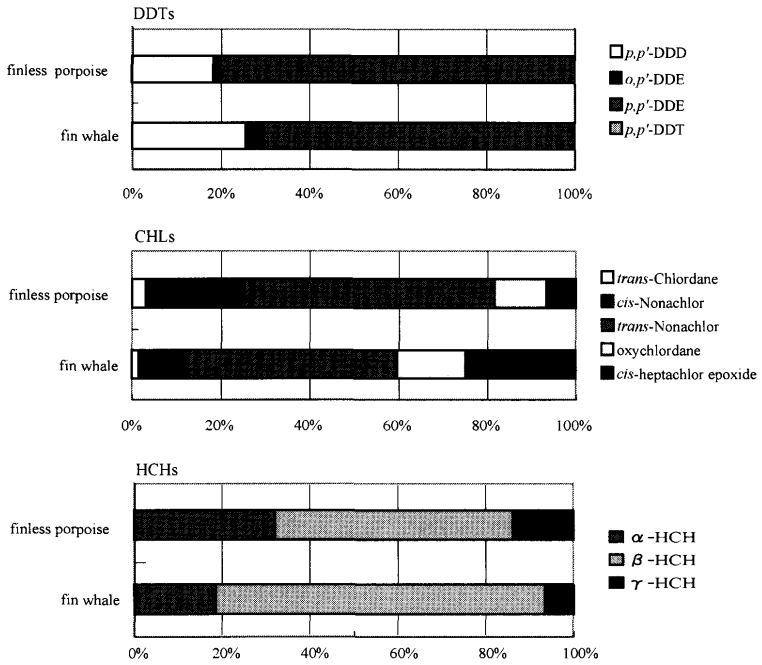

Fig. 2. Percentage composition of DDT compounds, CHL compounds, and HCH isomers in muscle sample of finless porpoise and fin whale.

concentrations in the whale and porpoise. The other possible explanation in POP concentrations between the whale and porpoise is that the fin whale is much larger (Lockyer 1976) and the amount of lipid that POPs dilute is relatively enormous (Borrell 1993).

With regard to ΣHCHs, their bioconcentration factor is lower than those of the other pollutants (Tanabe et al. 1984). This might explain why a lower concentration of ΣHCHs was detected in the finless porpoise than in the fin whale.

The other POP compounds, such as aldrin, endrin, and dieldrin, were not detected in samples from either mammal.

Concentrations of POPs in blubber, liver, and muscle of the finless porpoise

Concentrations of POPs in blubber and liver of the finless porpoise were also analyzed. The concentration range was 4.43–413.9 ng g^{-1} wet wt for blubber samples, and 0.06–7.48 ng g^{-1} wet wt for liver samples. Among the three components analyzed, blubber had the highest concentration level of POPs. The fat content for blubber, liver, and muscle samples were 89%, 3%, 2.5%, respectively. POPs are lipophilic, and therefore tend to accumulate in blubber.

Percentage composition of CHLs, HCHs, DDTs

Percentage compositions of DDTs, CHLs, and HCHs in muscle sample of finless porpoise and fin whale are shown in Fig. 2. For DDTs, *p,p'*-DDE was predominant in both finless porpoise and fin whale samples (79 and 70%, respectively); *p,p'*-DDD was 18 and 26%, respectively; and *p,p'*-DDT was detected only in the finless porpoise (0.7%). For CHLs, the sum of the metabolites *cis*-heptachlor epoxide and oxychlordane were 18% in finless porpoise and 40% in fin whale. For HCHs, the ratio of α-HCH and γ-HCH were smaller in the fin whale (19% and 6.4%, respectively) than in the finless porpoise (32% and 14%, respectively). On the other hand, the ratio of β-HCH was higher in fin whale (75%) than in the finless porpoise (54%). Since β-HCH is the most persistent HCH isomer, the ratio of β-HCH tends to increase at a higher level of the trophic level (Tanabe et al. 1984). In this case, much higher ratios of chlordane metabolites and β-HCH were found in the fin whale. This may indicate relatively greater metabolism of chlordanes and HCH isomers by fin whale. Also, it may indicate that the fin whale has greater exposure to β-HCH than the finless porpoise does throughout a typical life history.

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