D-2. 4 Environmental Monitoring of the World Oceans with Chemical Substances Accumulated in Squid Livers

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Abstract

The best way to find out a current state of marine pollution is to collect seawater samples and analyze them. But it is difficult to collect them from the world oceans and to analyze in very low concentration of pollutants. In squid livers various pollutants can be readily bioaccumulated. Using squid liver, we can monitor open seas where mussel watch can not cover.

About 30 species of squids around the Japan and from the world oceans, we determined the organotin compounds(TBT, TPT), PCBs, artificial radionuclides(^{60}Co, ^{108m}Ag, ^{110m}Ag), heavy metals, and PAH[(B(k)P, B(a)F, B(ghi)P] in livers. The concentration of those pollutants is higher in the northern hemisphere than in the southern hemisphere, and the highest near the Japanese waters. Bioaccumulation for TBT, PCB, and Co is estimated at about 10^{4-5} and Ag is estimated about 10^7.

Key Words Squid liver, Organotins, PCBs, PAH, Radionuclides, Heavy metals

1.Introduction

The oceans are the ultimate sink for anthropoganic pollutants. Marine organisms are able to accumulate certain elements and chemical substances from seawater in certain organs with their normal metabolism. This mechanism can be used to monitor marine pollution. Squid is a possible candidate for such an organism. To monitor marine polution, scientists in North America and Europe have been using Mytilus mussels since 1973 in a program well known as Mussel Watch. We have been examining the feasibility of using squid livers in a "Squid Watch" since 1991. The Japanese consume several hundreds of thousands of tons of squid, roughly half of the world catch, each year. Squid are collected from various areas around the world, and with careful analysis, we can use them as indicator organisms.

2. Research Objective

Squid can exist in the world oceans. It is carnivorous and is placed in high on the tropic level. Pollutants and elements which accumulate in the food chain are thus generally more concentrated in squid livers than in mussels. It is easy to remove the liver of a squid, but not the digestive glound from the soft parts of mussel. The liver of a squid, specifically the midgut gland, is analogous to the digestive gland of a mussel. The life span of squid is one year, so that pollutants in livers can reflect a current state of polution of the sea

3. Research Method

In Ommastrehpidae, 23 species are known in the world. Of those, 8 species are the object for catch by Japanese fisheries in Fig. 1. At first we have reviewed the ecology of these squid. We have collected and analyzed about 30 species around the Japanese waters and from the world. We have detected organotins(TBT, TPT), PCBs, artificial radionucleides(^{108m}Ag, ^{60}Co $^{239+240}Pu$), heavy metals and PHA[(B(k)P, B(a)F, B(ghi)P] in squid livers.

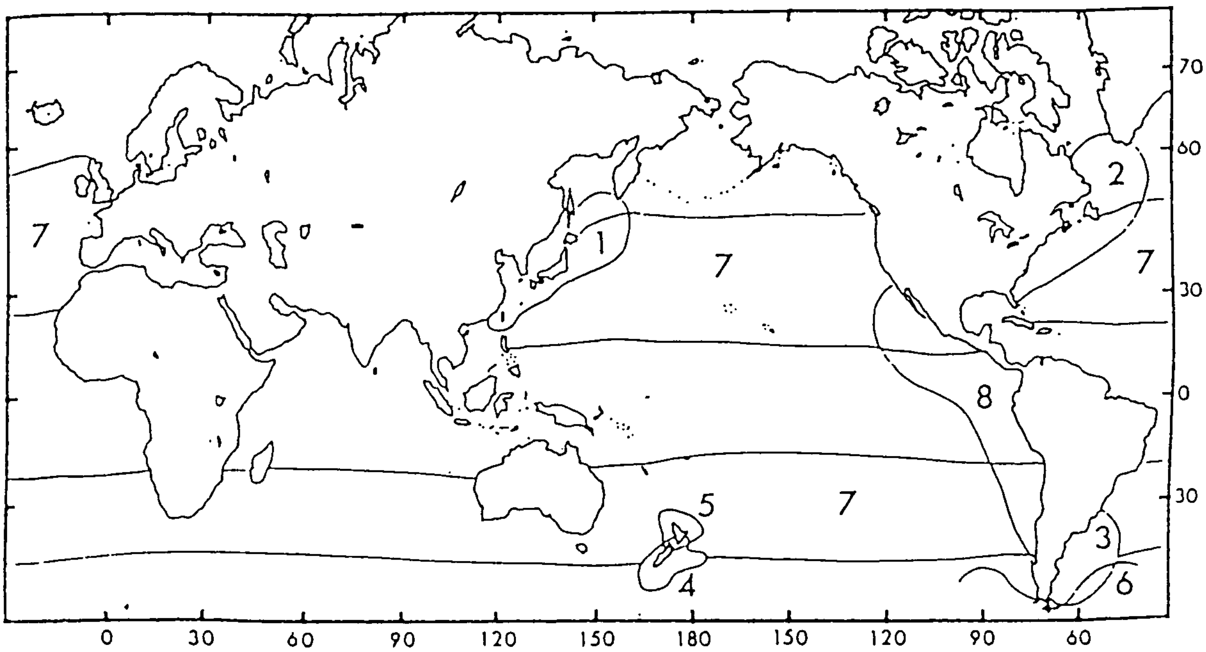

Fig. 1. Distributions of Ommastrephidae caught by Japanese fishing vessels.
1 : Todarodes pacificus, 2 : Illex illecebrosus, 3 : I. argentinus,
4 : Nototodarus sloani, 5 : N. gouldi, 6 : Martialia hyadesi,
7 : Ommastrephes bartrami, 8 : Dosidicus gigas. (Nakamura, 1993)

4. Results and Discussion

(1) Migration and liver composition

Squid, belonging to the family Ommastrephidae, are rather pelagic. The Japanese common squid[surume-ika], Todalodes pacificus, and neon flying squid[aka-ika], Ommastrephes bartrami, migrate far out in the sea, 3000 km or so. Australian squid, Nototodarus goulid, and New Zealand squid, N. sloani, do not migrate as far. Canadian illex, Illex illecebrosus, Argentine illex, I. argentinus, and Peru-Chilean giant squid, Dosidicus gigas, migrate over considerable distances. We believe that the contents of pollutants in squid livers reflect pollution over wide areas of the sea.

The liver of squid comprises 10% the body weight. Water content of livers is about 50%. Fat content is about 30%, and much of the fat contains fat-soluble compounds such as PCBs and TBT. Crude protein content is 20% and ash content is 1.3% on a wet basis. The major component(80%)of ash consists of oxides of P, Na, K and Cl as chlorides. A minor component(18%) consists of oxides of Mg, Ca, Sr, Fe, Cu, Zn and S. Most elements and radionuclides in seawater are indeed found in squid livers in concentrated form.

(2) Distribution of TBT, TPT, and PCBs

The concentrations of TBT, TPT and PCBs in squid livers of 16 species were determined. The

TBT concentration in livers of Sepia esculenta, Rossia pacifica and Watasenis scintillans was low compared to that of other species. The concentrations of TBT and TPT were not significantly different in the liver of Ommastrephidae. Ommastrephidae was suitable to the monitoring organisms. The TBT concentration in the squid livers depended on the TBT concentration in seawater, and it was high in the squid caught in the seawater of higher TBT concentration. The CF was estimated from the TBT concentration in seawater and the squid liver and it was 2×10^4 for TBT. The concentrations TBT, TPT and PCBs were high in squid liver caught in the Northern Hemisphere compared to those in the Southern Hemisphere. These distributions of TBT, TPT and PCBs concentration in livers apparently reflect the actual situation of marine pollution to a certain extent.

(3) Estimation and Distribution of ^{108m}Ag

About 200 results showed the level of stable Ag to be within a tenfold range(0.05-0.5 mg/g ash) among many species; however that of Co varied widely(D. gigas;0.1-0.5 mg/g ash, O. bartrami;0.03-0.3 mg ash, T. pacificus;0.01-0.03 mg/g ash, Heterololigo bleeker;0.002-0.01 mg/g ash). Assuming that the equilibrium of ^{108m}Ag/Ag remains quite stable between squid liver and sea water, ^{108m}Ag in seawater is estimated from ^{108m}Ag in liver as follows;

Stable Ag in liver / Stable Ag in seawater

= ^{108m}Ag in liver / ^{108m}Ag in seawater(=unknown)

= 1.3×10^7

Ag content in seawater:0.2 ng/kg ; average Ag in liver:2.6 mg/Kg wet(0.2mg/g ash x 1.3%) ; 2.6mg/0.2ng=1.3×10^7

Squid around the Japan contained 2-10 mBq/g ash. In 1979, no ^{108m}Ag was found in Australian squid in samples of sufficient ash(56g), even at a lower detection limit. In 1991, the value of ^{108m}Ag was 0.8mBq/g ash for New Zealand squid in neighboring water. For 12 years, the radiosilver has been slowly spreading within the water. Argentine illex and Martialia contained approximately 1.5 mBq/g ash, and this value was lower than that of the northern Canadian illex of 3.1 mBq/g ash. O. bartrami from the northern area(30-40'N) of the mid-North Pacific contained the highest levels, at 12-20 mBq/g ash in 1991-92 and 25-40 mBq/g ash in 1983. O. bartrami from the Atlantic contained 4-5 mBq/g ash, and off Peru, D. gigas contained 5-8 mBq/g ash. Higher levels of the radiosilver ^{108m}Ag were found in the Northern than in the Southern Hemisphere and possibly in the Pacific than the Atlantic Ocean. The specific radioactivity (S.R.: ^{108m}Ag[m,uBq/g]/Stable Ag[ug] per unit weight) could be accurately compared. Fig. 4. shows changes of S.R. of ^{108m}Ag and ^{60}Co in liver of T. pacificus in 1955-93. Now ^{108m}Ag content in seawater is estimated to be 4-6 mBq/g 10^3 tons of seawater and ^{60}Co to be 40-60 mBq/10^3. The peak of ^{110m}Ag in 1986 is correspond to the Chernobyl accident.

(4) Metals in Liver

The major components in liver is described before. Table 2 shows the median of the metal concentrations. By the correlation analysis, the significant relation are observed between Cu-Zn, Mn-Mo, Co-V. Mo-V, Mo-Co and Co-Cd. However, highly concentrated As and Ag in liver seemed to be accumulated independently.

(5) Determination of B(k)F, B(a)P, B(Ghi)P in liver

PHA were determined by CG-MS and HPLC-F method and Table 3 shows the results. Squid liver is very fatty and contained many inhibitors for PHA determination. It needs to inquire into further examination for monitoring PHA with squid liver.

Table 1. Organotins(TBT & TPT) concentratiuons in squid livers.

Fishing area	Species	Organotins concentration TBT (μg/g)	TPT
Toyama bay	Sepia esculenta	0.034±0.006	0.218±0.004
	Rossia pacifica	0.050±0.008	0.448±0.159
	Sepioteuthis lessoniana	0.091±0.017	0.281±0.073
	Heterolotheigo bleekeri	0.228±0.047	0.185±0.062
	Nipponolologo japonica	0.378±0.089	0.461±0.068
	Watasenia scintillans	0.064±0.003	0.099±0.006
	Berryteuthis magister	0.606±0.208	0.261±0.060
	Todarodes pacificus	0.219±0.050	0.312±0.098
	Thysanoteuthis rhombus	0.162〜0.178	1.267〜1.468
The Northwest Pacific (39-59 N) (152-59 E)	Onchoteuthis borealijaponica	0.053±0.018	0.050±0.013
	Gonatopsis borealis	0.063±0.014	0.073±0.014
	Todarodes pacificus	0.051±0.013	0.049±0.011
(40-58 N) (152-01 E)	Todarodes pacificus	0.044±0.006	0.033±0.010
(41-45 N) (150-29 E)	Ommastrephes bartrami	0.033±0.003	0.039±0.010
(40-48 N) (150-39 E)	Ommastrephes bartrami	0.031±0.008	0.016±0.002
The North Atrantic (Franch water)	Loligo vulgaris	0.036±0.012	0.085±0.004
	Illex coindeti	0.010〜0.011	nd〜0.002
	Todaropsis eblanae	0.016±0.006	0.004±0.003
	Todaropsis sagittatus	0.015	0.023

nd : not detected.

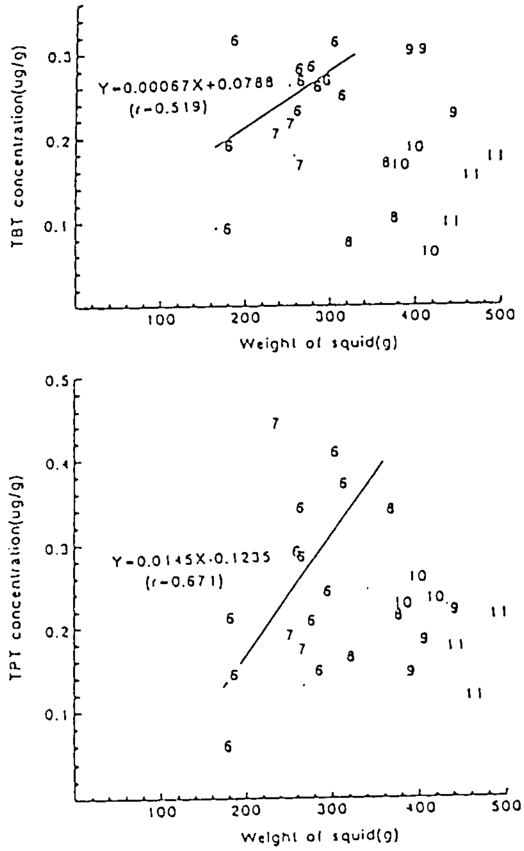

Fig. 2. Correlations squid weight with TBT or TPT concentrations in squid livers.

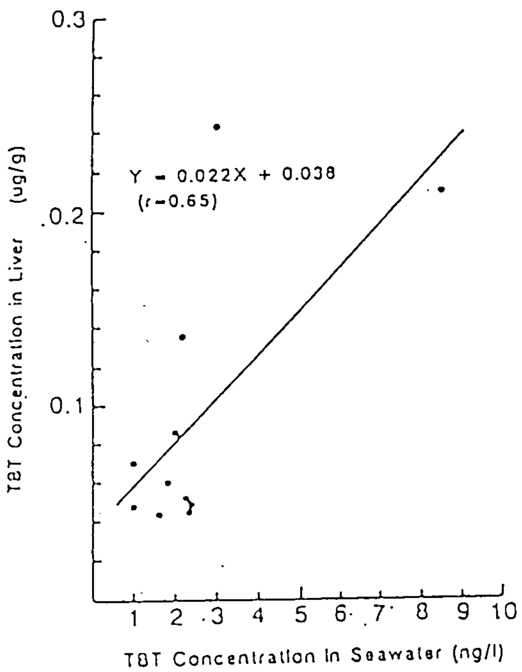

Fig. 3. The correlation TBT concentration in seawater with TBT concentration in squid liver.

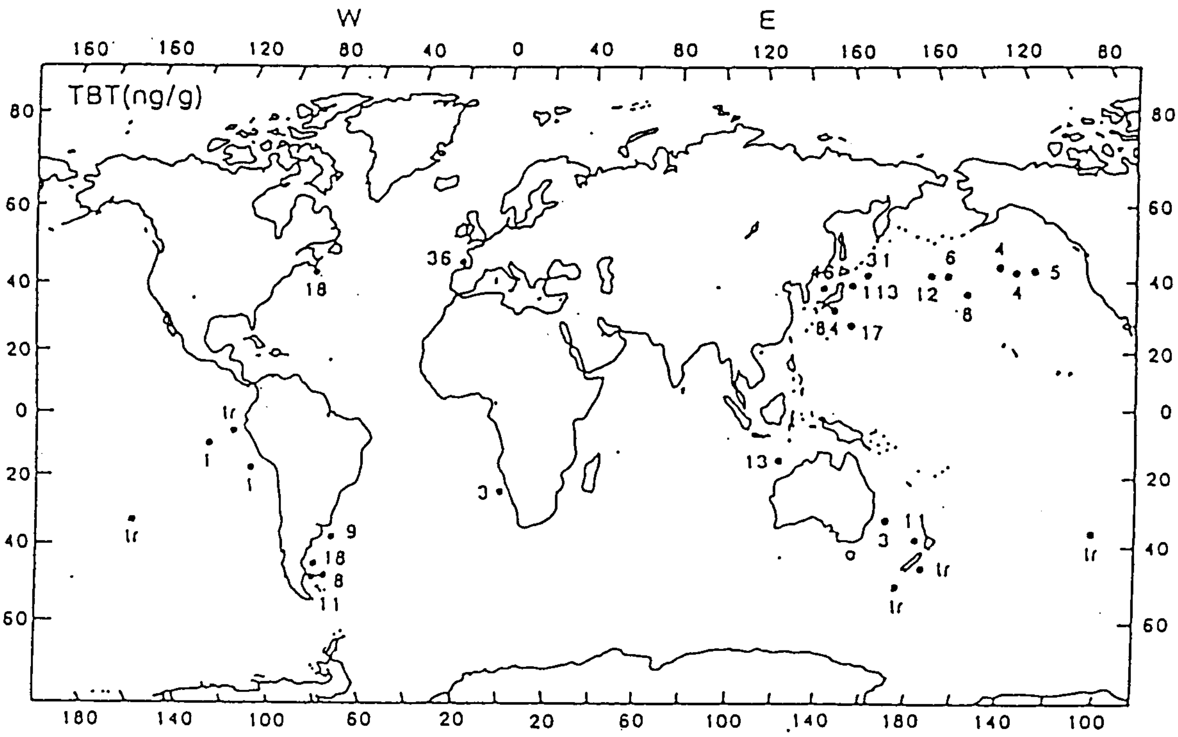

Fig. 4. TBT concentrations in squid livers in the world.
tr : < 1 ng/g.

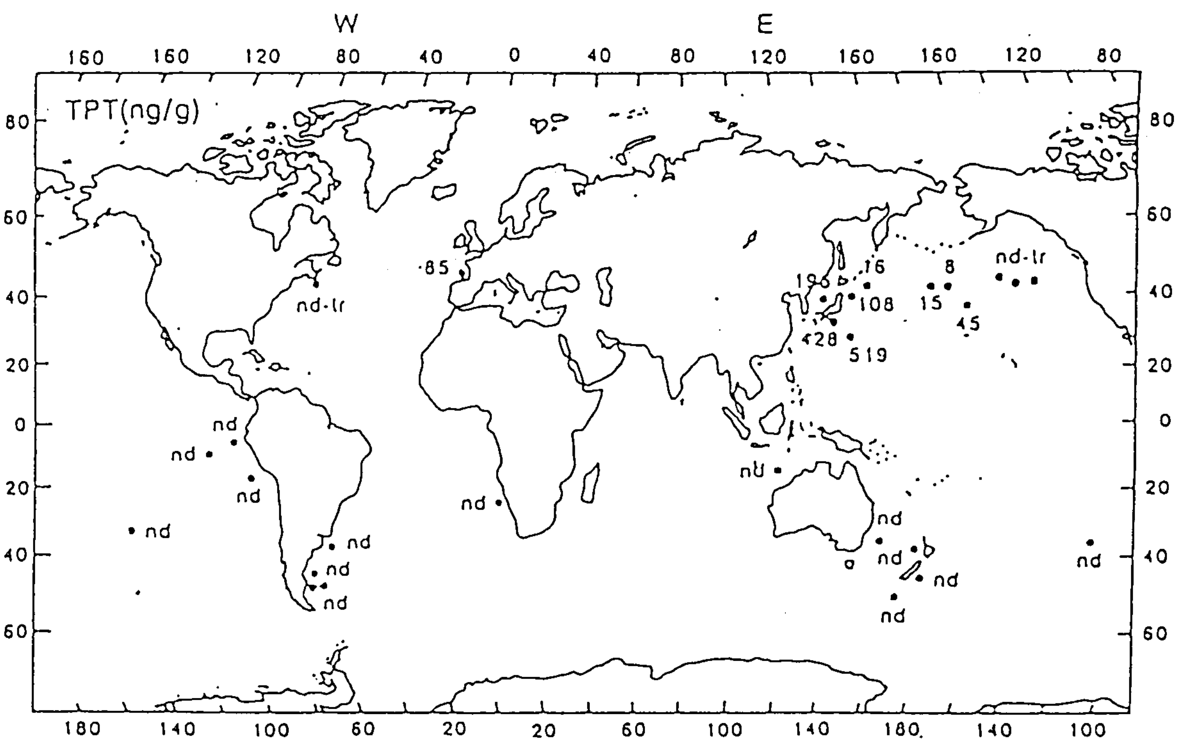

Fig. 5. TPT concentrations in squid livers in the world.
nd : not detected, tr : < 1 ng/g.

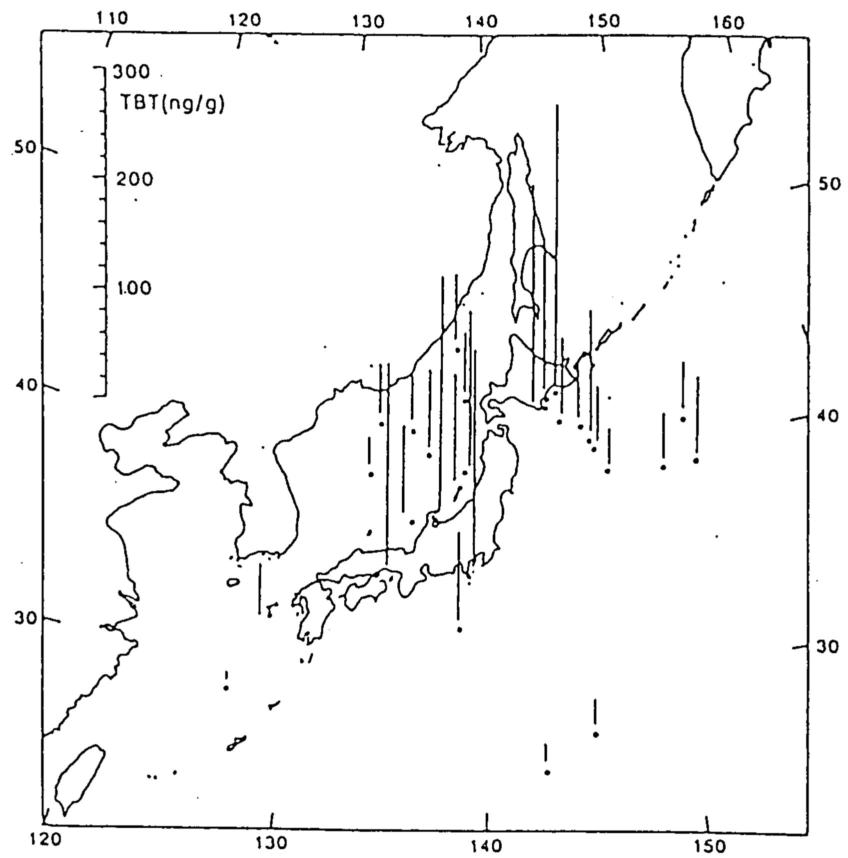

Fig. 6. TBT concentrations in squid livers around the Japan.

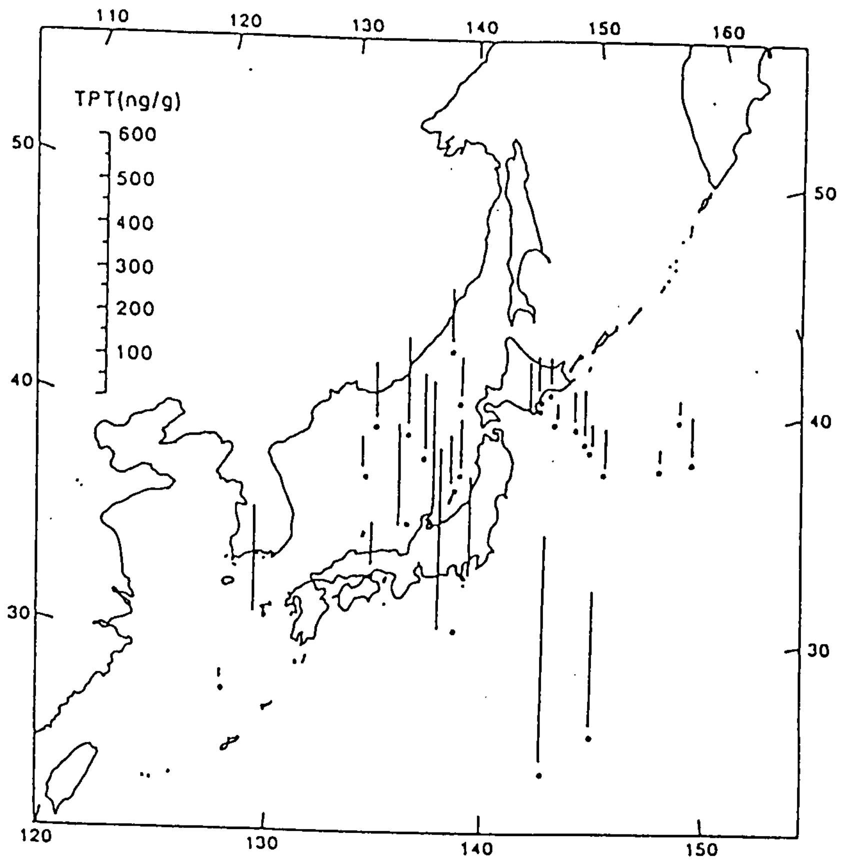

Fig. 7. TPT concentrations in squid livers around the Japan.

(6) Experimental Cd uptake by S. lessoniana(oval squid)

In liver of D. gigas and I. argentinus ,400ppm(400mg/Kg wet) of Cd is contained, although Cd function is unknown. We have reared S. l. for 100 days with success, fed with live small crustaceans and fishes, after hatching of naturally spawn eggs. Young squid(20-80g) were exposed in Cd seawater(0.1mg/l) and depurated for 2 weeks(uptake via seawater). Next youngs were maintained in Cd seawater with live mammichog as food (uptake via seawater + food). Biological half-life of Cd was estimated to be 20-24 days via seawater only or via seawater+food. By the compartment model analysis, Cd content attains the maximum at 50g body weight, and decreases hereafter until 1/2 of the maximum at 200g.

5. Summary

(1) Squid of the Ommastrephidae are distributed over the world oceans and several species are caught by the Japanese fishing vessels. They are adequate species to monitor the marine pollution of the open seas where mussel do not inhabit.

(2) In squid liver, PCBs, TBT, TPT, ^{108m}Ag, and ^{60}Co, are highly accumulated. These concentrations are the highest in the midlatitudes of the Northern Hemisphere and less in the Southern Hemisphere.

(3) With only 10 individuals (wet weight of liver 200g), we can determine PCBs, TBT, TPT, and with 10-30kg squid can do ^{108m}Ag, ^{60}Co.

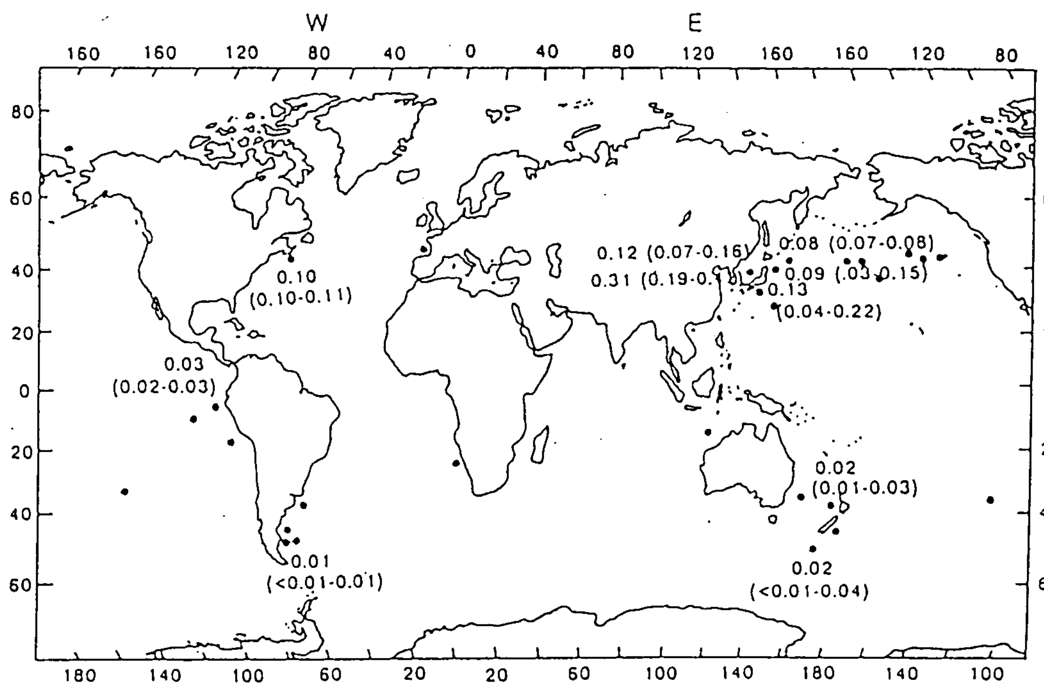

Fig. 8. PCBs concentrations in squid livers in the world.
PCBs : μg/g wet.

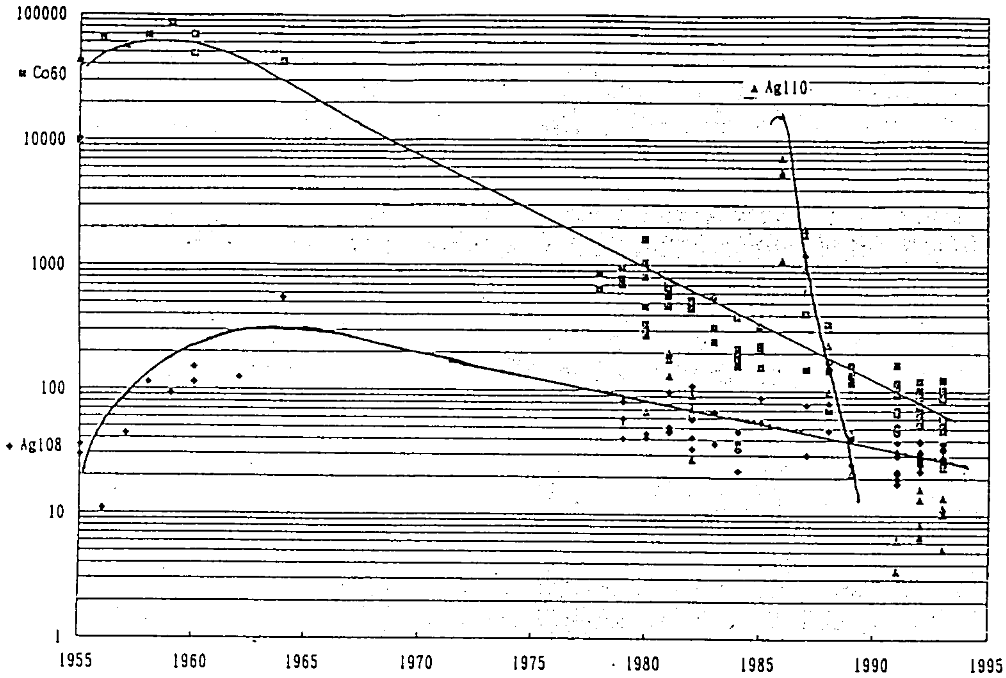

Fig. 9. Chronological specific radioactivity of ^{108m}Ag, ^{110m}Ag, and ^{60}Co in Japanese flying squid(T. pacificus)

Table 2. The median of metal concentrations in squid livers. (n=49、unit : mg/kg wet wt.)

Elements	Median(Min. −Max.)	Elements	Median(Min. −Max.)
Mg*	380 (190-600)	As	4.0 (2.2-12)
Ca*	160 (53-460)	Rb	1.3 (0.67-2.0)
V	0.45(0.07-26)	Sr*	3.1 (0.87-7.6)
Mn	1.1 (0.55-1.9)	Mo	0.45(0.11-1.4)
Fe*	130 (38-340)	Ag	1.0 (0.15-4.7)
Co	0.88(0.07-5.6)	Cd*	62 (1.7-400)
Ni*	1.2 (<1.0-9.9)	Pb	0.14(<0.05-1.4)
Cu*	150 (6.6-650)	U	0.06(0.02-0.49)
Zn*	68 (19-240)		

* : determined by ICP-AES, others : determined by ICP-MS

Table 3. PHA concentrations in squid liverds (ng/g liver(wet weight))

Species	Fishing area(n)	B(k)F	B(a)P	B(ghi)P
S. oualaniensis	Indian Ocean(2)	n.d.	0.005-0.008	n.d.
T. pacificus	Japan sea(3)	0.185-2.775	0.017-0.206	n.d.-0.550
	off Sanriku(3)	0.341-0.462	0.020-0.029	n.d.-0.059
	off Izu Oshima(3)	n.d.-0.805	0.020-2.427	n.d.-0.605
	New Zealand water(3)	n.d.-0.075	0.004-0.019	n.d.-0.046
O. bartrami	The North Pacific(2)	0.386-0.492	0.060-0.565	n.d.
	Tasman sea(1)	n.d.	0.027	n.d.
S. lessoniae	off Goto Islands(1)	n.d	0.066	n.d.
O. borealijaponica	The North Pacific(3)	n.d.	0.006-0.022	n.d.