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MERCURY CONTENT OF COPEPODS (CRUSTACEA) COLLECTED FROM THE ANTARCTIC SEA*

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Abstract: Inorganic and methylmercury in copepods collected from 9 stations in the Antarctic Sea in December 1985 and February 1986 was measured. There was considerable variation of inorganic mercury in copepods at all stations while inorganic mercury in copepods from deeper (bottom) waters was higher than that from surface waters. This result indicates that the inorganic mercury concentrated in the copepods might have been derived from bottom sediments and/or bottom waters. On the contrary, there is little regional or vertical difference in methylmercury content of copepods which was generally low. Its value is considered to be standard value in sea areas expected to be non-polluted from human activities. The mercury content (mean value) in zooplankton collected from various sea areas was compared with each other. The value of total mercury in the Antarctic Sea (recorded in the present study) was about the same as that in Yatsushiro-kai adjacent to polluted area and was higher than those in the other non-polluted sea areas, except the East Indian Ocean (off Java) affected by active submarine volcanos.

1. Introduction

Much information on the mercury content of zooplankton has become available (COCOROS *et al.*, 1973; HIROTA, 1979; HIROTA *et al.*, 1974, 1979, 1983a; HONDA *et al.*, 1983; KAMATA and TSUBOTA, 1983; KNAUER and MARTIN, 1972; SKEI *et al.*, 1976; TAKEDA and KATAOKA, 1984; ZAFIROPOULOS and GRIMANIS, 1977). However, in most of the previous works, the whole samples collected by a plankton net have been used for analysis. Therefore, it is likely that clay and detritus may have been included in the samples collected in coastal waters. Furthermore, mixed samples containing various taxonomic groups differing with respect to water content are not suitable for comparing mercury contents on a dry weight basis. Hence, it is essentially requisite to analyze the mercury content of specific taxonomic groups (such as copepods, it being a dominant group in zooplankton community) separated from the mixed zooplankton sample. We collected zooplankton in the Antarctic Sea, sorted out the copepods, and measured their mercury content.

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2. Materials and Methods

Samples were collected at 9 stations (4 stations in Breid Bay, 2 stations in Gunnerus Bank, and 3 stations in Lützow-Holm Bay) in the Antarctic Sea (Fig. 1), in December 1984, and February 1985, during the JARE-26 cruise. Samples were taken by horizontal tow using an MTD plankton net made from processed bolting silk GG54 (aperture 0.328 mm), at about 50, 90, 130, 170, 210 and 250 m in depth. For mercury analysis, these were divided into two groups: one is a mixture of samples from 50, 90 and 130 m (surface layer) and the other those from 170, 210 and 250 m (deep layer). Collected samples were immediately preserved in a 10% formalin in sea water, and brought back to the laboratory. Mercury in formalin was not detected. In the laboratory, copepods were sorted and removed by a pair of chopsticks with stainless steel needles attached to their ends. The copepods were rinsed with distilled water on a silk gauze and dried in an oven at 60°C to obtain a constant weight. The dried materials were stored in a desicator, after that methylmercury and inorganic mercury content were determined.

Methylmercury in copepods was analyzed as follows: A sample or a standard solution was accurately put into a conical flask with a ground stopper to be immersed in 30 m*l* of 1N-hydrochloric acid solution for 24 h. The acid solution thus treated was filtered along with 20 m*l* of 1N-hydrochloric acid solution through a silk gauze and into a 200 m*l*-separating funnel. The hydrochloric acid solution was shaken with 25 m*l* of benzene for 10 min using a mechanical shaker. After the solution was clearly separated, the acid layer was transferred to an another 200 m*l* separating funnel. Twenty-five m*l*

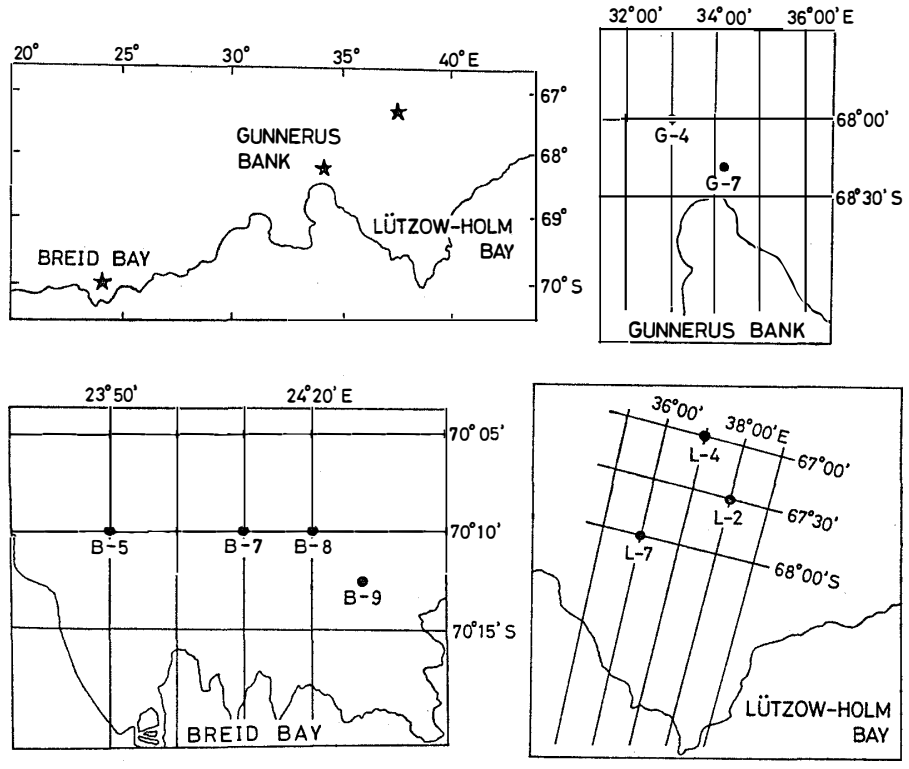

Fig. 1. Map showing the sampling locations in the Antarctic Sea.

of benzene was added to the acid solution. After shaking for 10 min, the acid layer was removed and the residual benzene layer was mixed with the former benzene layer. The hydrochloric acid contained in the benzene mixture was washed out by shaking with 15 m*l* of 20 (w/v)%-sodium chloride. This washing procedure was repeated three times. The cleaned benzene layer was shaken with 5 m*l* of 0.05(w/v)%-glutathione solution for 5 min. The glutathione layer was transferred to a 30 m*l* conical flask with a ground stopper. The residual benzene layer was shaken again with 5 m*l* of 0.05(w/v)%-glutathione solution for 5 min and the latter glutathione layer was mixed with the former glutathione layer in the conical flask. One m*l* of concentrated hydrochloric acid and 2 m*l* of benzene were added to the mixed glutathione solution and the mixture was shaken for 2 min. After the hydrochloric acid layer was removed, the benzene layer was dehydrated with sodium sulfate anhydrate and used as the sample for measuring by gas chromatography. After the measurement, 2 m*l* of 0.05(w/v)%-glutathione solution was added to the sample for measuring, they were shaken together and the final sample for measuring was measured again so as to confirm that the target peak of methylmercury chloride disappeared in the chromatogram.

Inorganic mercury in copepods was analyzed as follows: The residue left from the methylmercury extraction or a standard solution was put into a round-bottom ashing flask. The content in the flask was treated with nitric acid and then it was digested with sulfuric acid and potassium permanganate. Mercury in the digested solution was measured by flameless atomic absorption spectrophotometry (Sugiyama-gen MV-253R) (HIROTA *et al.*, 1983b).

Total mercury content of copepods is the sum of methylmercury and inorganic mercury concentrations.

3. Results and Discussion

The mercury content of copepods at each station is shown in Table 1. The values of inorganic mercury considerably changed from station to station. The highest value

Table 1. Mercury content of copepods collected in the Antarctic Sea (ppm, dry weight basis).

Station	Date	Inorganic mercury		Methylmercury	
		Surface	Deep	Surface	Deep
B-5	Feb. 11, 1985	0.25	0.38	0.029	0.024
B-7	Dec. 27, 1984	0.033	0.085	0.044	0.026
B-8	Dec. 29, 1984	0.006	0.056	0.040	0.024
B-9	Dec. 30, 1984	0.074	0.25	0.025	0.022
G-4	Feb. 22, 1985	0.19	0.26	0.033	0.037
G-7	Feb. 25, 1985	0.15	0.32	0.021	0.057
L-2	Feb. 3, 1985	0.095	0.16	0.028	0.021
L-4	Feb. 4, 1985	0.23	0.35	0.017	0.033
L-7	Feb. 5, 1985	0.82	1.2	0.016	0.023

Detectable limit: Inorganic mercury 0.0001 ppm
Methylmercury 0.0005 ppm

(1.2 ppm) was recorded at the deep layer of St. L-7 in Lützow-Holm Bay on February 5. The value of total mercury at this station was the highest among the values investigated in the various sea areas expected to be non-polluted from human activities. The lowest value (0.006 ppm) was at the surface layer of St. B-8 in Breid Bay on December 29, and the value of total mercury at this station (0.046 ppm) was equal to the value of copepods from the Antarctic Sea reported by HONDA *et al.* (1983). These results may indicate the high variability in mercury content of marine organisms inhabiting the Antarctic Sea. The values of inorganic mercury of copepods collected from the deep layer were higher than those from the surface layer, at all stations. This may suggest that the inorganic mercury concentrated in the copepods was derived from bottom sediments

Table 2. Mercury content of zooplankton collected in various seas (ppm, dry weight basis).

	Total mercury mean (*n*)	Methylmercury mean (*n*)	Authors
Japanese waters			
Minamata Bay*			
(1972)	(Z) 1.553 (4)	0.449 (4)	HIROTA *et al.* (1974)
(1979–1986)	(C) 1.253 (41)	0.188 (32)	HIROTA *et al.* (unpubl.)
Yatsushiro-kai			
(1972)	(Z) 0.297 (6)	0.251 (6)	HIROTA *et al.* (1974)
(1979–1980)	(C) 0.114 (10)	0.062 (9)	HIROTA *et al.* (1983a)
Ariake-kai			
(1972)	(Z) 0.169 (3)	0.147 (3)	HIROTA *et al.* (1974)
(1973)	(Z) 0.182 (9)	—	HIROTA (1979)
(1980)	(C) 0.085 (2)	0.042 (2)	HIROTA *et al.* (1983a)
Setonaikai	(C) 0.055 (5)	0.031 (4)	HIROTA *et al.* (1983a)
Kagoshima Bay	(Z) 0.110 (6)	—	KAMATA and TSUBOTA (1983)
East China Sea	(Z) 0.219 (1)	0.077 (1)	HIROTA *et al.* (1974)
Tropical Pacific Ocean	(Z) 0.058 (17)	0.013 (7)	HIROTA *et al.* (1979)
Eastern Pacific Ocean			
Off shore	(Z) 0.119 (26)	—	KNAUER and MARTIN (1972)
Open ocean	(Z) 0.130 (16)	—	KNAUER and MARTIN (1972)
Western Atlantic Ocean			
Core Sound	(Z) 0.13 (4)	—	COCOROS *et al.* (1973)
Oyster Bay	(Z) 0.11 (4)	—	COCOROS *et al.* (1973)
Mediterranean Sea			
Elefsis Bay	(C) 0.29 (7)	—	ZAFIROPOULOS and GRIMANIS (1977)
East Indian Ocean			
Off Java	(Z, W) 0.493 (12)	—	TAKEDA and KATAOKA (1984)
Off Sumatra	(Z, W) 0.173 (28)	—	TAKEDA and KATAOKA (1984)
Norwegian fjord*	(M) 6.277 (11)	—	SKEI *et al.* (1976)
Antarctic Sea			
"Krill"	(W) 0.028 (1)	—	HONDA *et al.* (1983)
"Copepoda"	(W) 0.046 (1)	—	HONDA *et al.* (1983)
"Copepoda"	0.30 (18)	0.029 (18)	present study

* Polluted sea area, (*n*): sample number, (C): Copepoda, (Z): zooplankton consisting various taxonomic groups, (M): mixed sample of zoo- and phytoplankton, (W): value converted from wet weight basis.

and/or bottom waters. On the contrary, there is little regional or vertical difference in methylmercury content of copepods which was generally low (below 0.06 ppm). These values were close to values of copepods from the Tropical Pacific Ocean and Setonaikai (Inland Sea of Japan) (HIROTA *et al.*, 1979, 1983a). Such values of methylmercury are considered to be standard value in sea areas expected to be non-polluted from human activities.

In Table 2, the mercury content on dry weight basis (mean values in each investigation) of zooplankton investigated in various sea areas is shown. Though these values were derived from samples consisting of only one (Copepoda or Krill) or various taxonomic groups and values analyzed on dry or wet weight basis, they are hardly comparable with each other. In this table, the values reported on wet weight basis were converted to dry weight basis, using the percentage of water content of zooplankton as 85%. In the artificially polluted areas (Minamata Bay and Norwegian fjord), the mean values of total mercury content of zooplankton were very high (above 1 ppm). It is rather high in Yatsushiro-kai adjacent to polluted Minamata Bay. In non-polluted areas, the mean values were undoubtedly low compared with those in the two above-mentioned polluted sea areas. Among them, the value in the East Indian Ocean (off Java) was higher than those in the other regions. The value in the Antarctic Sea was about the same as that in Yatsushiro-kai adjacent to polluted area. TAKEDA and KATAOKA (1984) inferred that active submarine volcanoes may have an important effect upon the mercury content of plankton collected off Java. The cause of high mercury content of copepods in the Antarctic Sea is still unknown. Detailed studies are further needed to understand the causative factor for the high mercury content of Antarctic copepods.

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