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Total and Organic Mercury in Marine Fish of the Upper Gulf of Thailand

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Mercury compounds are utilized on a large scale both in industry and agriculture. Mercury from industrial wastes accumulate in soil and water, and may be translocated to the aquatic environment, which in turn becomes a source of contamination of fish. The ability of some micro-organisms to methylate inorganic mercury to the more biologically stable alkyl forms and the more toxic forms further increases the danger of contamination (MENASVETA 1975). Recently, high levels of mercury were found in fish from Swedish lakes and streams. The principal mercury contaminant of these fish was reported to be an organic form of methyl mercury (JOHNELS et al. 1967, WESTOO 1966).

In 1975, the total mercury contents in fish of the gulf of Thailand reportedly ranged from 0 to 0.58 ppm (NATIONAL MARINE SCIENCE COMMITTEE 1976). In a recent study (MENASVETA 1976), traces of total mercury were found in the marine food chain, which tend to increase at higher trophic levels and according to the animal's size. As Thailand is one of the countries where the nationwide fish consumption is comparatively high, further study on the contamination of organic mercury in fish is essential.

MATERIALS AND METHODS

Samples for mercury analysis were collected from the upper Gulf of Thailand (Figure 1). Fish samples were collected from the catch of otter trawl. Trawlings were done in September 1976 and March 1977. The species of fish from which samples were taken ranged from the lower trophic level to the higher trophic levels. Plankton samples were collected by a plankton net. All of the samples were preserved in a freezer at approximately -20 C. For assay the fish were thawed and dissected with a stainless steel knife, and a portion of muscle under the dorsal fin was used for mercury determination.

Total mercury levels in the fish were determined by means of the flameless Atomic Absorption technique. One gram of muscle tissue was digested in 25 mL of 1 : 1 concentrated redistilled HNO_3 and concentrated H_2SO_4, and further oxidized with 10 mL of saturated $K_2S_2O_8$ solution. Excess oxidizing agents and mercury ions were reduced by 20 mL of reducing solution (20 g $NH_2OH.HCl$, 33g $SnCl_2 . 2H_2O$, 1g hydrazine sulfate, and 9 mL concentrated H_2SO_4 dilute to one L), and the mercury was vaporized

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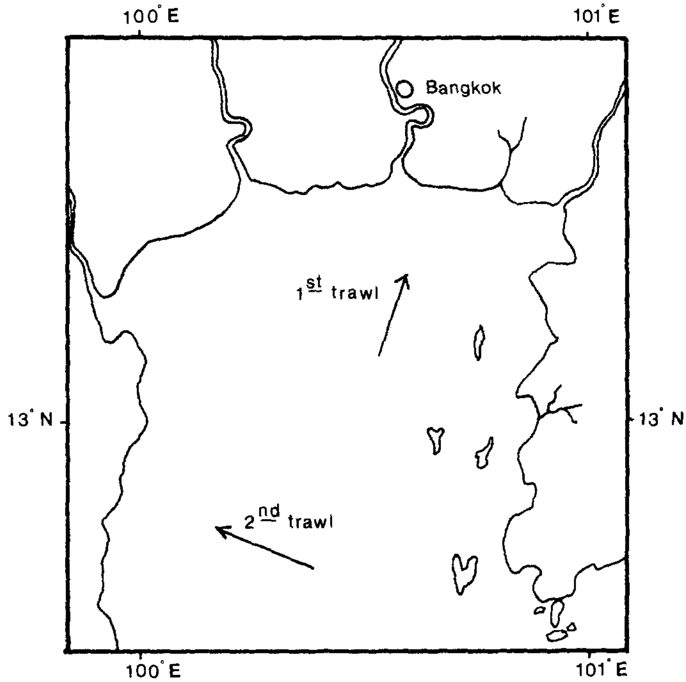

Figure 1 The upper Gulf of Thailand and the sites of trawling for fish samples.

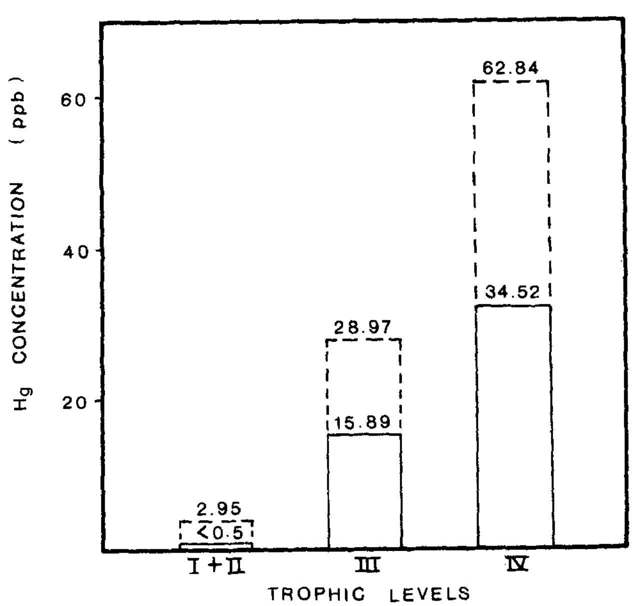

Figure 2 Mean of Total and Organic mercury concentration in the four trophic levels.

in the flameless Atomic Absorption apparatus.

The analytical procedure for the measurement of organic mercury was adapted from the UTHE et al. (1972). The sample (2g) is mixed and shaken for 30 min with 20 mL of $CuSO_4$ (0.1 M) solution and 10 mL of acid solution [H_2SO_4(5N), NaBr(3M)]. The mixture is filtered afterwards through glass wool and the whole is rinsed with 10 mL of bidistilled water. The aqueous phase is transferred to a separatory funnel and extracted with 20 mL of benzene. After separation of the phases, the benzene and the emulsions formed are collected in a tube and centrifuged at 3000 rpm for 20 min. A part of the benzene phase is collected. Two mL of thiosulfate solution [95% ethanol - 0.005 M $Na_2S_2O_3$ in water, (1 + 1)] are added to the benzene phase. After shaking, the phases are centrifuged and the aqueous solution of methyl mercuric thiosulfate is transferred with the help of a Pasteur pipet to a 250 mL Erlenmeyer flask containing 100 mL of acid solution (HNO_3 1000 mL + H_2SO_4 100 mL dilute to 1 L), 10 mL of saturated $K_2S_2O_8$ solution and 50 mL of distilled water. The flask contents were mixed and allowed to stand for 15 min. Twenty mL of reducing solution (20g $NH_2OH.HCl$, 20g NaCl, 33g $SnCl_2.2H_2O$, 1g hydrazine sulfate, and 9 mL concentrated H_2SO_4 diluted to one L) were added to the sample, which was immediately aerated to volatilize the reduce mercury into the flameless Atomic Absorption instrument.

RESULTS AND DISCUSSION

One hundred and ninety-one samples of 22 species of fish, 27 samples of 2 species of crustacean and 10 samples of plankton from the upper Gulf of Thailand were analysed for total and organic mercury. The results are shown in Table 1. All results were reported on the wet weight basis. Total mercury concentrations were found ranging from 2 to 650 ppb with the mean value of 41 ppb. Organic mercury ranged from 0 to 280 ppb with the mean value of 23 ppb.

Of the total 228 samples analysed, 82% contained total mercury concentration of less than 50 ppb, 11% had a total mercury content between 50 - 100 ppb and 7% contained over 100 ppb. According to MENASVETA (1975), these concentration could be regarded as a natural background of mercury for fish in general. It should be noted that only 2 samples were found having total mercury levels above the United States Food and Drug Administration tolerance limit of 500 ppb.

As regards organic mercury, 91% of the samples analysed contained less than 50 ppb of organic mercury and 6% of the samples contained between 50 and 100 ppb. Only 3% of the samples contained organic mercury in concentrations higher than 100 ppb.

Table 2

Total mercury and organic mercury contents in the four trophic levels.

Trophic levels	No. of Samples	Total mercury (ppb)			Organic mercury (ppb)		
		range	mean	standard deviation	range	mean	standard deviation
I, II	10	2 - 5	3	1	0 - 1	0.5	0.01
III	129	2-130	29	20	1 - 56	16	11
IV	89	10-650	63	110	4-280	35	54

Table 2 gives the mean, range and standard deviation of total and organic mercury concentrations in the four trophic levels. The mean value of total mercury and organic mercury of the first and second trophic levels (composited species of plankton) was 3 ppb and 0.5 ppb, respectively. The mercury residue concentration in the third trophic level was higher than the first and second trophic levels. The mean value was 29 ppb for total mercury and 16 ppb for organic mercury. The mean value of the fourth trophic level was 63 ppb for total mercury and 35 ppb for organic mercury. Student 't' test showed a significant difference in total and organic mercury concentrations between trophic levels I + II and trophic level III and between trophic levels III and IV ($P < 0.5$). The highest mercury residue (650 ppb) was detected in Lutianus malabaricus (malabar snapper). This species was categorized in trophic level IV.

According to the above analysis, it can be concluded that there is a biological magnification of mercury residue. Fish of higher trophic levels bear higher mercury residue than those in the lower trophic levels (figure 2). This suggests that mercury may be concentrated in the same manner as an organic compound such as organochlorine compounds, i.e., passed through and amplified by the food chain. The concept appears correct when considering the data presented by JOHNELS et al. (1967), SCOTT and ARMSTRONG (1972), and MENASVETA (1976).

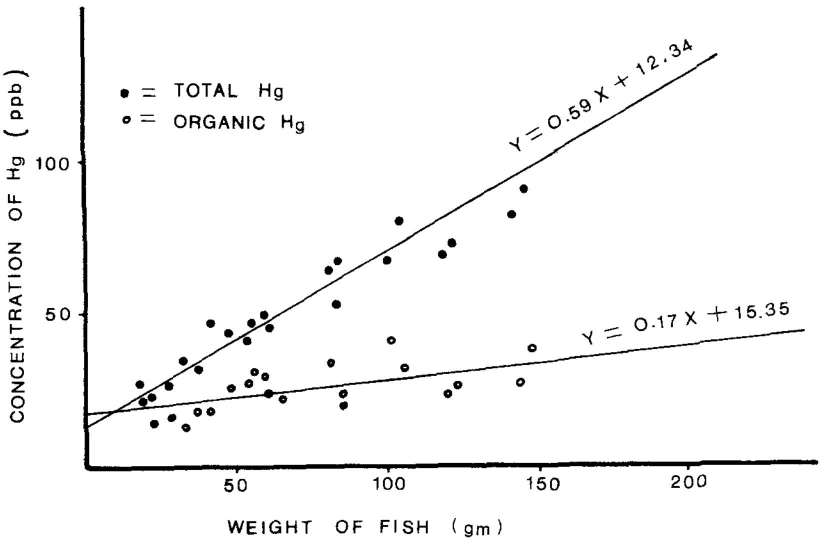

Figure 3 The relationship of Total Hg and Organic Hg to the weight of *Caranx gymnastethoids*

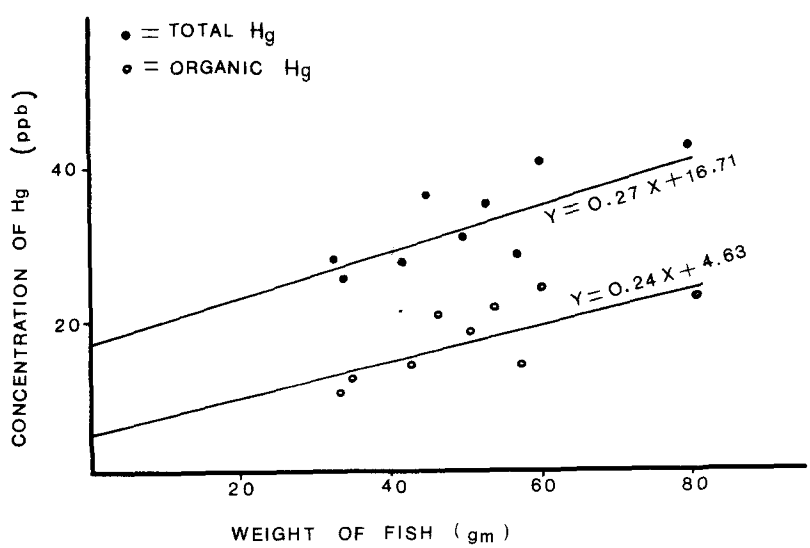

Figure 4 The relationship of Total Hg and Organic Hg to the weight of *Rastrelliger neglectus*

The statistical analysis revealed the positive linear regression between the size of the fish (weight) and mercury contents (both total and organic) of 19 species of fish. Figures 3 and 4 give the example of the linear regression in Caranx gymnastethoids (barebreast trevally) and Rastrelliger neglectus (chub mackeral), respectively. The positive linear regression between age/or weight and mercury contents of fish is well documented (SCOTT and ARMSTRONG 1972, MENASVETA and SIRIYONG 1977).

The proportion of organic mercury to total mercury found in this investigation ranged from 41% to 72%, with a mean of 58%. These proportions were similar to the proportion detected in fish of the South China Sea as reported by MIYAMA and TOYAMA (1973).

As regards the variations in organic mercury proportions in each species of fish and shellfish, the covariance analysis revealed that, there were two types of variation, i.e.,

1. the proportion decreased as the fish size increased, e.g., Figure 3,
2. the proportion remained constant as the fish size increased, e.g. Figure 4.

The first type of variation might be due to the rapid uptake of inorganic mercury, i.e., the accumulation of inorganic mercury was faster than the methylation. RIVERS et al. (1972) also found that the proportion of organic mercury in Pacific blue marlin decreased as the weight of the fish increased.

It should be noted that the proportion of organic mercury in plankton was less than 20%. This low proportion might be due to the inability of phytoplankton to methylate mercury, as reported by MATIDA (1972).

The results of this study indicated that the average mercury content of fish from the upper Gulf of Thailand was lower than the United States Food and Drug Administration tolerance limit of 500 ppb. The mean value of 41 ppb for total mercury is only one-twelfth of this tolerance limit.

However, it is probably not practical to consider this recommended level without correlating it to the frequency of consumption. At present, the fish consumption rate among Thai people is 20 kg/person/ year (MARR et al. 1976). This level is equal to 55 g/person/day. If the mean total mercury content of fish and shellfish is 41 ppb, it can be calculated that the daily intake of mercury through fish consumption is 2.3 µg/person/day for Thai people. This value is lower than 4 µg/person/day as reported from Sweden (NILSSON et al. 1972) and greater than 2 µg/person/day as reported from England (ANONYMOUS 1971). The Joint FAO/WHO Expert Committee on Food Additives proposed that the provisional tolerate-weekly intake (PTWI) of mercury for man be set at 0.0033 mg/kg body-weight for methyl mercury (ANONYMOUS 1972). This value is equal to PTWI of 0.2 mg. mercury as methyl mercury, for an average body-weight of 60 kg. The daily mercury intake of 2.3 µg/person/day which we derived from this study, would contribute to the weekly intake of

Table 1

Total and Organic mercury contents in analysed samples

Scientific name	Common name	Trophic level	No. of Samples	Total mercury (ppb)		Organic mercury (ppb)	
				range	mean	range	mean
1) Composited species of plankton	Phyto and Zoo plankton	I,II	10	2-5	3	0-1	0.5
2) Caranx gymnastethoids	Barebreast trevally	III	23	19-130	55	11-56	28
3) Rastrelliger neglectus	Shortbodies mackerel	III	11	23-40	31	9-25	18
4) Megalopsis cordyla	Torpedo trevally	III	6	10-26	18	7-14	10
5) Rastrelliger kanagurta	Rakegilled mackerel	III	11	15-31	24	6-16	11
6) Parastromateus niger	Black pomfret	III	9	5-61	30	4-32	18
7) Caranx leptolepis	Slender trevally	III	15	10-69	32	8-35	20
8) Pentapus setosus	Tickletall	III	8	22-46	33	9-27	14
9) Upeneus tragula	Blackstripe goatfish	III	10	6-22	12	5-15	6
10) Siganas oramin	Whitespotted spinefoot	III	9	29-35	32	21-27	23
11) Peneaus sp.	Marine shrimp	III	12	2-16	11	1-10	6
12) Loligo sp.	Squid	III	15	6-27	14	3-17	8
13) Scomberomous Commersoni	Barred Spanish mackerel	IV	7	65-150	97	40-66	54

TABLE 1 (CONTINUED)

Scientific name	Common name	Trophic level	No. of Samples	Total mercury (ppb)		Organic mercury (ppb)	
				range	mean	range	mean
14) *Saurida tumbil*	Greater lizardfish	IV	10	18-37	27	11-26	18
15) *Lutianus malabaricus*	Malabar snapper	IV	7	46-650	220	28-280	106
16) *Dasyatis zugei*	Pale-edged stingray	IV	9	10-28	17	4-19	9
17) *Priacanthus tayenus*	Spot finned bigeye	IV	6	31-66	44	16-46	27
18) *Scolopsis cancellatus*	Lattice monoclebream	IV	12	21-36	28	16-22	19
19) *Johnius argentalus*	Silver johnfish	IV	5	13-20	17	9-13	11
20) *Elagatis bipinnalatus*	Rainbow runner	IV	5	33-58	42	11-27	21
21) *Nemipterus hexodon*	Sixtooth threadfin	IV	15	20-40	26	14-25	18
22) *Epinephelus tauvina*	Greasy grouper	IV	5	69-160	95	20-55	44
23) *Rachycentron canadus*	Cobia	IV	2	99-290	190	74-180	130
24) *Chilocyllium indicum*	Ridge-back catshark	IV	5	81-480	240	52-190	120
25) *Notuma thalassinus*	Giant Catfish	IV	1	510	510	260	260
Total			228	2-650	41	0-280	23

0.016 mg/person (via fish only). Therefore, this level is only one-twelfth of the PTWI of mercury (assuming that all mercury contributed by fish is in the form of methyl mercury).

The result of this study indicates that the mercury levels of fish from the upper Gulf of Thailand are within the safety limit. However the situation may change in the future, because at present our country is still at a developing stage. Modern agricultural techniques, including extensive use of pesticides, coupled with industrial development, will substantially increase the amount of mercury in the environment in the future. Hence the plan for proper protection and control of mercury residue in Thailand's environment should be formulated and implemented without delay.

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