High Ethylmercury in River Fish by Man-made Pollution

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In the nation-wide survey of mercury levels in river fish conducted by the Ministry of Health and Welfare (later by the Environment Agency) since 1968, the authors have collaborated with the project by analysis of samples in several districts.

Unusually high levels of mercury around 1 ppm were found in fish from the Shokotsu and the Muka Rivers (in Hokkaido), the Jinzu and the Oyabe Rivers (in Toyama Pref.), the Hono River (in Nara Pref.), in addition to the notorious Minamata Bay and the Agano River, where human poisoning incidents have been reported.

In the Jinzu River, the extraordinary feature was the detection of ethylmercury in fish far above the level of methylmercury. To identify the source of the pollution, mercury in fish was analyzed at different locations along the river. Finally, investigation implicated a pharmaceutical factory synthesizing an antiseptic "Thimerosal" (Sodium ethylmercury thiosalicylate) which was discharging ethyl- and inorganic mercury into the river. This was probably the first time that pollution by ethylmercury was detected. The source of pollution was then eliminated by dredging the drainage and the bottom of the river. Human poisoning from organic mercury was thus prevented. But the mercury content in the fish did not readily decrease. In this report, the authors report the alteration in mercury level in the fish following the dredging.

Materials and Methods

From 1968 to 1973, many fish, dace (Tribodon hakonensis) and ayu (Plecoglossus altivelis), were collected from 10 to 17 spots in the Jinzi River in Toyama Prefecture.
Muscle tissue of fish was analyzed. The total mercury level in fish was determined by a method that was developed utilizing the flameless atomic absorption technique (LIDUMS 1967, LEONG 1971, NISHI 1974). The quartz sample boat containing 10 to 200 mg of muscle tissue and about 0.5g of calicium hydroxide as neutralizing agent was put in a quartz furnace. The sample was decomposed completely by heating it at a temperature of 850°C for 5 minites in an oxygen stream. Mercury vapor was caught on a gold trap. After finishing the sample combustion, the gold trap was immediately heated at a temperature above 850°C. Mercury vapor was released from the gold trap and analyzed by flameless atomic absorption.

Instrument; Sugiyamagen MV-250 Mercury Vapor Matic
Toshiba-Beckmann Mercury Vapor Meter MV-253

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Organic mercury in the fish samples was determined by a modification of gas chromatographic method developed by WESTÖÖ (1967) and SUMINO (1968). A one to five gram sample of fish was weighed and transfered into a 50ml centrifuging tube with 3 N hydrochloric acid and benzene. The organic mercury was extracted into the benzene layer, and the benzene extract was injected into a Shimazu GC-4BEP apparatus, fitted with a ^{3}H-foil electron capture detector and a 150 cm glass column (ϕ4 mm) containing 5 % HIEFF on chromosorb W HMDS, 80 to 100 mesh. The carrier gas (N_2) was maintained at a flow rate of 30 ml/min and the component temperatures were set at 170°C, 200°C and 200°C for the oven, the injector and detector respectively.

Results and Discussion

1) Investigation of the Source of Pollution

In our survey on mercury levels in river fish in 1968, high ethylmercury above 1 ppm was found in fish from the Jinzu River, but the source was not evident. Our first hypothesis was that the pollution might be of a geological nature. Then in 1969, the authors surveyed mercury levels in river fish from the branches of the Jinzu River and the upper stream. The results are shown in Fig. 1. High mercury levels in fish were not detected from the Yamada, Muromaki, Miya and Takahara Rivers, which are the names of the upper streams of the main Jinzu River. But downstream in the Jinzu River and its branch rivers, the Kumano and Ida Rivers, high ethylmercury levels in fish were found locally.
In particular, the percentage of ethylmercury was extraordinarily high as around 80 %, being far above the methylmercury level.

The authors then thought the source might be of man-made origin. The local goverment re-checked all factories along the river and found a factory synthesizing an antiseptic "Thimerosal" (Sodium ethylmercury thiosalicylate). The reaction used to produce it was the following:

$$C_2H_5MgBr + HgCl_2 \longrightarrow C_2H_5HgCl \longrightarrow C_2H_5HgOH$$

$$C_2H_5HgOH + \text{C}_6\text{H}_4(\text{SH})(\text{COOH}) \longrightarrow \text{C}_6\text{H}_4(\text{SHgC}_2\text{H}_5)(\text{COOH}) \longrightarrow \text{C}_6\text{H}_4(\text{SHgC}_2\text{H}_5)(\text{COONa})$$

The history of Thimerosal production in the factory is shown in Fig.2. Production began in October of 1964, and abruptly increased in 1968. Mercury in waste water was treated to deposit it as mercuric sulfide for recovering the metal. It appeared that the waste water treatment procedure became inefficient with increase of production, and much inorganic and ethyl-mercury was discharged into the Kumano River.

According to the report of KAWASAKI et al. (1974), total mercury levels in the bottom mud were 9300 μg/g in the drainage and 2300 μg/g in the Kumano River near the waste outlet. This pollution level was very high, about the same as that in Minamata Bay.

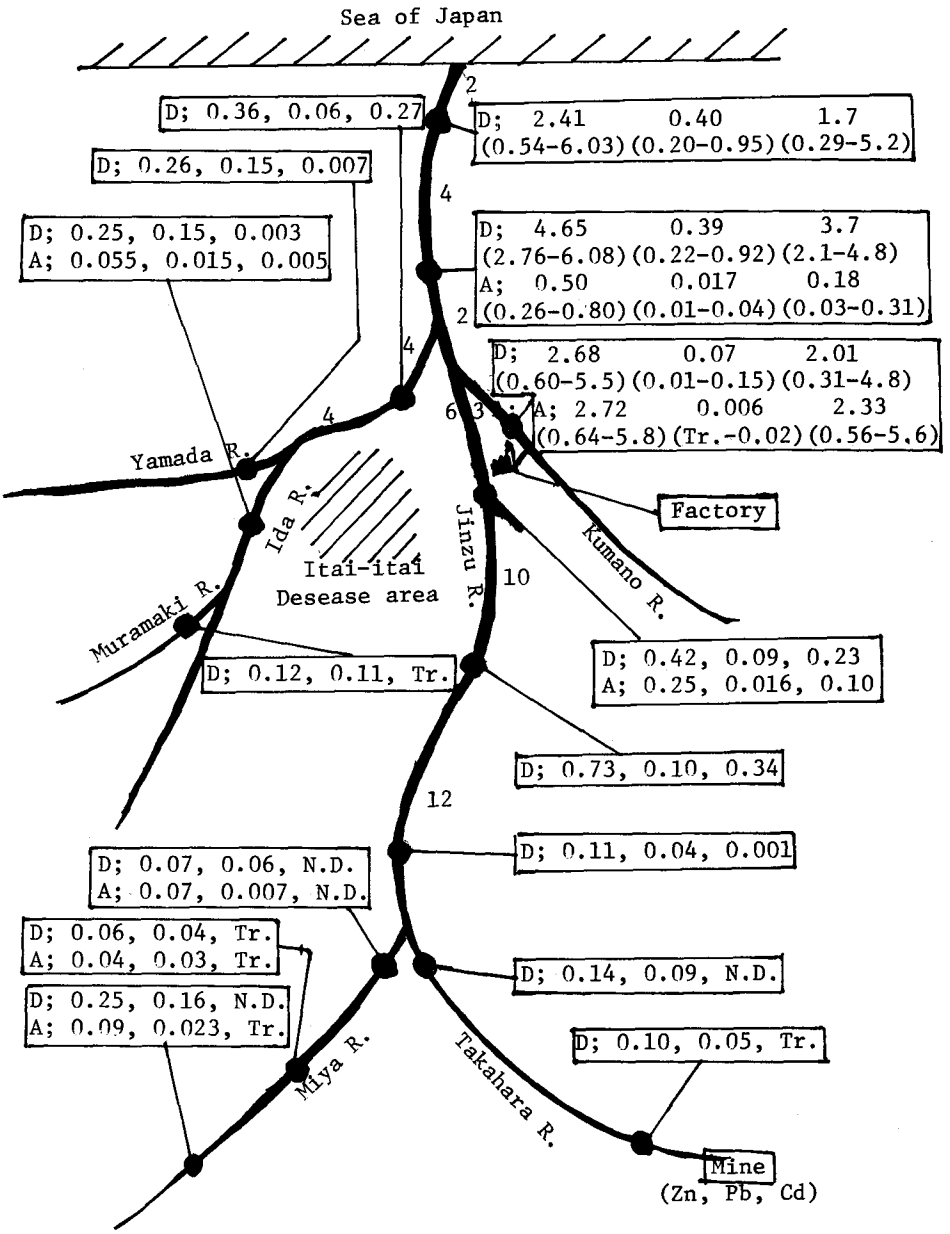

Fig.1. Mercury Levels in Fish from the Jinzu River (1969)

Total mercury, Methylmercury, Ethylmercury

D; Dace, A; Ayu, The average (Range), ppm on a wet basis.
The figures along the river indicate the distance(km)

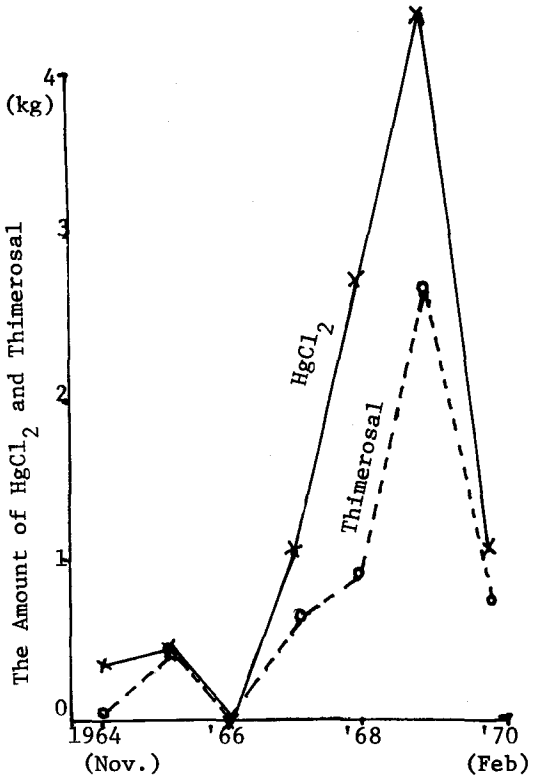

Fig. 2. The Amount of $HgCl_2$ Used and Thimerosal Production in the Factory

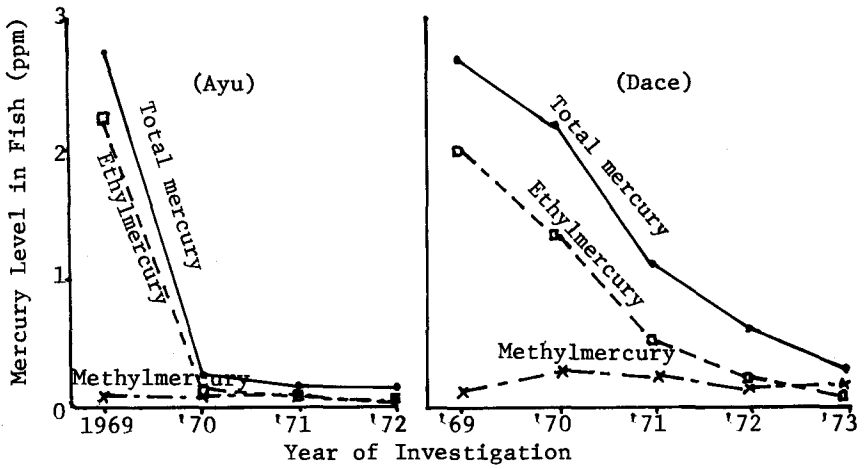

Fig.3. Changes in Mercury Levels in Fish

2) Follow-up Survey

The highly polluted bottom mud was eliminated by dredging the drainage and the river in May of 1970. Mercury levels in fish from the river were periodically surveyed for 4 years. The results are shown in Fig. 3. A difference was found in the pattern of decreasing mercury level between the dace and ayu. The ayu is fish with a one-year life span which comes up the river in Spring. So the mercury level in the ayu was almost as low as the control level the next year after dredging because the fish of that year were new-comers. It was thought that the mercury level in ayu reflected the present mercury pollution level in the river.

On the other hand, the mercury level in dace, which is a popular river fish in Japan and lives for several years, did not decrease readily. It took one and a half years for the mercury level in dace to be reduced to half. Therefore after 4 years, the mercury level in dace finally dropped to the control level. The fact proves again that the biological half life of mercury in fish is very long in the natural environment also (MIETTINEN 1968, JÄRVENPÄÄ 1971, YAMANAKA 1974a). Dace which were living more than 10 km from the source of pollution were contaminated by ethylmercury, suggesting the distance that contaminated fish can travel.

Mercury level in fish from man-made contamination in the river differed from that in the geologically contaminated river (YAMANAKA 1974b). The pollution of the former was local, but that of the latter was widespread. In the former, a heavy fluctuation in mercury level in individual fish was found, and the correlation between mercury level and size of fish was as shown in Fig. 4. In the latter, it tended to be the reverse.

This survey of mercury contamination in the Jinzu River led to the following conclusion:

1) This was the first incident in which fish were found to be contaminated by ethylmercury from industrial waste water.
2) The river pollution could be detected and the suspected spots might be identified by analyzing the mercury level in river fish.
3) Alkyl mercury pollution continued in the fish for several years, even though the source of pollution was eliminated.
4) The pattern of mercury contamination in fish from a man-made source, as found in the Jinzu River, was different from that in fish contaminated by natural geological sources.

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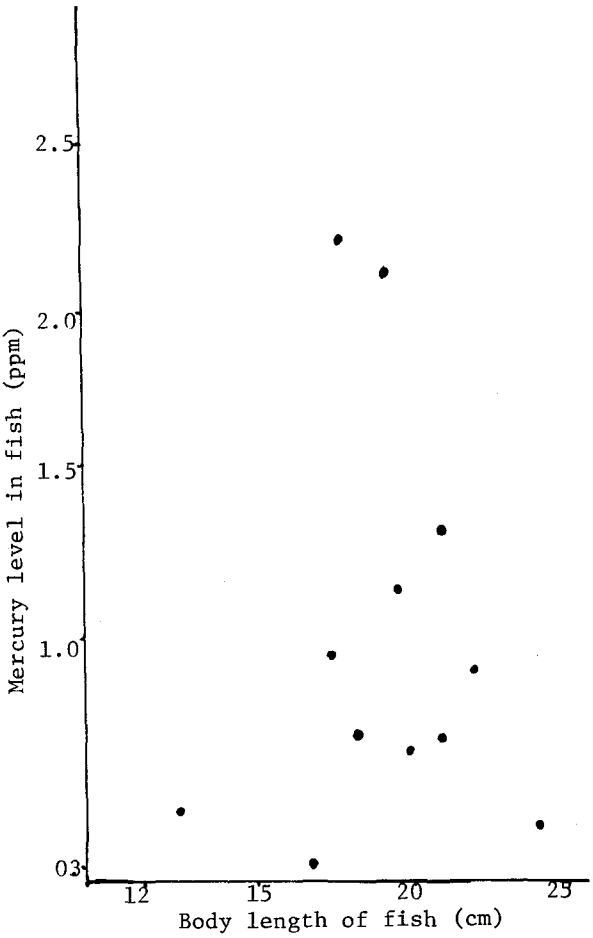

Fig.4. Correlation between Mercury Level and Fish Size