THE TOTAL MERCURY CONCENTRATIONS IN FISH FROM CERTAIN SOUTHERN COASTAL WATERS AND NORTH SOLOMONS PROVINCE OF PAPUA NEW GUINEA.

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ABSTRACT

Total mercury concentrations using potassium permanganate digestion in barramundi fish (Lates calcarifer) from Western Province were found to be higher than those from Gulf province. Some individual barramundi from Western province had total mercury levels in the excess of the WHO recommended limit of 0.50 micrograms per gram (ug/g) based on wet weight (WW). Jewfish or croakers (Sciaenidae) and threadfins salmon (Polynemidae) from Gulf province had mercury concentrations within the acceptable limit. Mercury levels in one area was quite high. The mackerel (Scombridae) fish from Mullins Harbour, Milne Bay Province had their mercury levels ranged from 1.81 - 3.59 ug/g WW and the mean concentration was 2.60 ug/g WW. Some of the barramundi caught in the Mullins Harbour had also been found to have mercury concentrations above 0.50 ug/g WW.

Key words: *Barramundi fish (Lates calcarifer), jewfish or croakers (Sciaenidae), threadfins salmon (Polynemidae), mackerels (Scombridae), mercury concentrations, flameless atomic absorption spectrophotometer, cold vapour generation unit.*

INTRODUCTION

The importance of mercury in the food system has become better understood in recent years. Inorganic and organic mercury derivatives from anthropogenic sources or as effluent from industrial wastes end up in the sediment of lakes and rivers. These derivatives are converted by chemical reactions or by the action of microbes into the organic compounds such as methylmercury, which are very poisonous to animal life (Goldwater 1971; Kyle and Ghani 1981; Hord *et al.* 1990).

Methylmercury, unlike the inorganic form is soluble and is transported downstream to the sea and can be taken in by the organisms such as fish, in which it may accumulate to high levels. Mercury poisoning of fish predators can occur by metallic mercury and its inorganic salts and organic mercurial compounds (Clarke and Clarke 1975; Hord *et al.* 1990).

Mercury poisoning derived from environmental and industrial sources reached major prominance in relation to human health at Minamata Bay, Japan in the early 1950's and has been referred to since then as Minamata disease (Goldwater 1971; Kyle and Ghani 1981; Kyle 1984). It is now recognised that the use of mercury compounds in Agriculture and Industry can cause dramatic increases in mercury levels in living organisms both on land and in water (Clarke and Clarke 1975; Kyle and Ghani 1981; Hord *et al.* 1990). The most common source of mercury poisoning in man is fish.

There have been several incidents of mercury poisoning reported other than in Japan. These include incidents in the Middle East, Asia, Europe, Central and North America have led to the setting up of international controls on safe levels of mercury in fish for human consumption. (Goldwater 1971; Bakir *et al.* 1973; Hord *et al.* 1990). Fish can aquire mercury from two possible pathways, via the food chain or by direct extraction from the water across gill tissue (Clarke and Clarke 1975; Kyle and Ghani 1981). Most of the mercury form, which accumulates in fish is present in the more toxic methylmercury, because it has an ability to diffuse across cell membranes and has high fat solubility (Kyle and Ghani 1981).

The symptoms of mercury poisoning in human have been described by Petr 1978/79; Holdsworth 1975; Kyle and Ghani 1981.

Fish form a major part of the diet of a large number of coastal people in Papua New Guinea, and are an

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important export. (Kyle and Ghani 1981). The Papua New Guinea Government earns revenue of some millions of kina per annum from export of marine products. Export protocols require testing of fish samples for mercury. This is necessary to ensure that the minimum mercury level required by the destination country is not exceeded. This paper presents data derived from such analytical tests for mercury conducted at the National Veterinary Laboratory on marine products destined for export market and local consumption over a period of four years (1986-1989).

MATERIALS AND METHODS

The fish analysed were caught by commercial fishing companies during the period of 1986-1989. Most came from the mouth of the Fly river and Daru waters of Western Province, Baimuru area of Gulf Province, Yule Island waters of Central Province and Mullins Harbour of Milne Bay Province. In addition a few fish were caught in waters of the Kieta area of North Solomons Province (Fig 1, Table 1).

The fish were delivered to the laboratory as whole or filleted frozen specimens from time to time by inspectors of the Department of Fisheries and Marine Resources. A few fish specimens were received from Provincial Health Inspectors (Fig 1).

The total number of fish samples received for mercury analysis were 228, ranging in numbers from 3 from North Solomons Province to 130 from Gulf Province. The species of fish included barramundi (*Lates calcarifer*), jewfish or croakers (Sciaenidae), threadfins salmon (Polynemidae), mackerel (Scombridae) (Kan *et al.* 1989; Matsuoka *et al.* 1991) and a small number of unidentified edible fish (Table 1). Also analysed was a single mud crab (*Scylla serrata*) from Baimuru area in Gulf Province.

The Equipment

A Varian model AA-475 Atomic Absorption Spectrophotometer (AAS) was used at the wavelength of 253.7 nanometer (nm). The settings of AA-475 were double beam and peakheight with absorption mode used for reading the absorbance. The slit width (spectral Band width) and a single mercury lamp current were set at 0.5 nm and 4.0 nm respectively. A Varian model 65 Vapour Generation Unit was placed on a convenient position close to the AAS and the inert gas (nitrogen) connected to it at a pressure of 1.4 KG/CM^2. The flow-through mercury cell assembly was inserted into the burner mount and aligned with optical path in the AAS (Okuno *et al.* 1972; Brodie 1979). A Varian model 9176 Recorder was also used to record the peakheight readings.

Sample Digestion

The digestion method was described by (Meir 1976). Duplicate samples 2.0-5.0 grams (g) of fish muscle was weighed into clean 125 millilitre (mL) graduated Erlenmeyer flasks. About 20 mL of AR grade nitric acid was added and digested at room temperature with occasional swirling to break the lumps of sample and left over night. On the following day 40 mL of 5 percent (w/v) potassium permanganate solution was added with occasional swirling to reduce frothing. An additional 2.0 g of solid potassium permanganate was added to samples which were high in fat. The mixture was left overnight again for digestion to continue. An extra 20 mL of permanganate solution was added on the following day and the mixture placed in a 60°C waterbath for 30 minutes, which destroyed any remaining froth. The flasks were removed from the waterbath and placed in a tray with cold water to cool rapidly to room temperature and 6-10 mL of hydroxylamine solution was added to remove excess permanganate and manganese oxide. The solution was made up to 100 mL with the distilled water and analysed for mercury using an atomic absorption spectrophotometer equipped with a hydride vapour generation unit.

Spiked samples with known concentrations were prepared with each batch of tests to calculate full percentage recovery. The same procedure was followed with standard reference materials, namely dried ground dogfish' and agalfish* muscles. (Kacprzak and Chvojka 1976; Brodie 1979; Evans *et al.* 1986).

All glassware used had been previously soaked overnight in a hot solution containing one percent potassium permanganate and 5 percent (v/v) sulphuric acid. On the following day the solution was discarded and hydroxylamine solution added to remove the excess permanganate. Finally the

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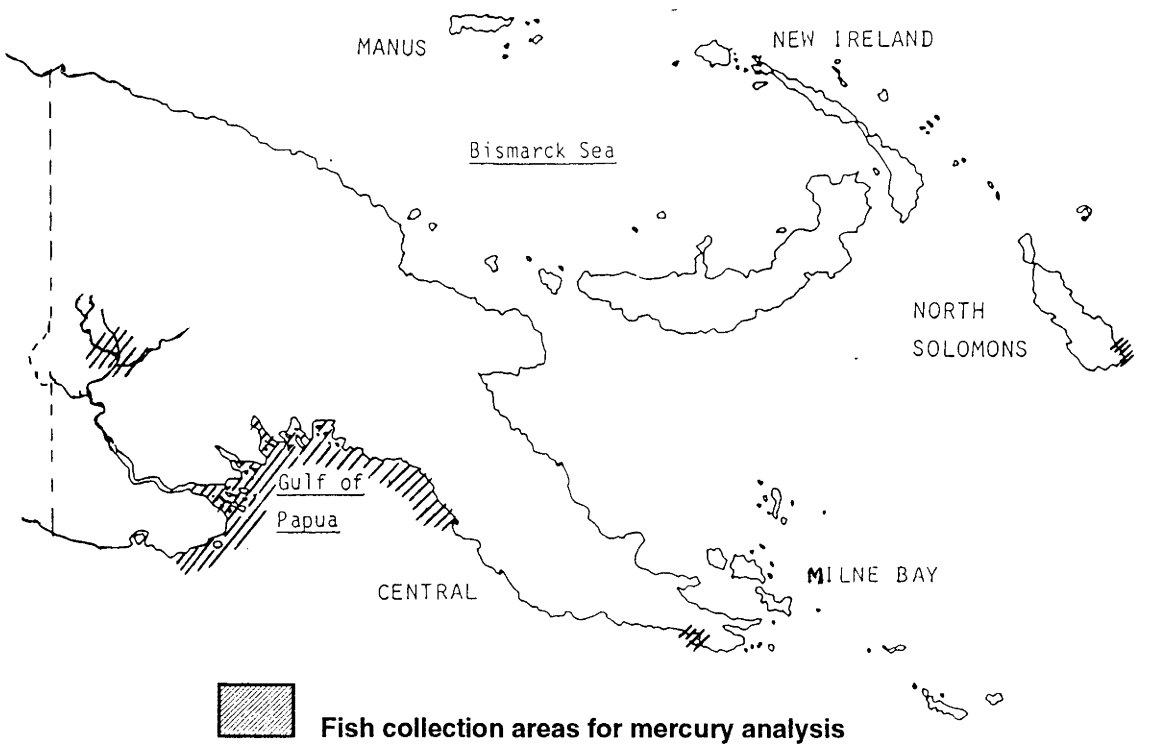
Figure 1. **Map of Papua New Guinea**



glassware was thoroughly rinsed with distilled water and dried in an oven.

Standard Preparation and Sample analysis

A stock mercury solution of 1000 ug/ml mercuric nitrate, Spectrosol, British Drug House (BDH) was used for mercury standard. An intermediate mercury standard of 0.10 ug/ml was made up with 5 percent (v/v) nitric acid, AR grade. The working standard mercury solutions of 1, 2, 4, 8, 12 and 16 ng/ml were prepared with 5 percent (v/v) nitric acid.

The AAS was calibrated to zero absorbance before reading the standard and sample solutions. Twenty millilitre (mL) of the blank, standard or sample solution was added the reaction vessel of the cold vapour generation unit. One millilitre of stannous chloride solution (w/v) was injected through the septum and the magnetic stirrer switched on for 90 seconds. The inert gas was purged through the reaction vessel to transport the mercury vapour into the flow-through cell. After an integration period of 10 seconds, the absorbance and peak height were read simultaneously. The reaction vessel was thoroughly cleaned with distilled water before the next sample was analysed using the same procedure.

RESULTS

The mercury concentrations of the two reference standard materials analysed were 0.843 ug/g $\pm$ 0.079 ug/g WW for dogfish and 0.49 ug/g $\pm$ 0.6 ug/g WW for agalfish. The values are in close agreement with the manufacturers values of 0.798 ug/g $\pm$ 0.074 ug/g WW for dogfish and 0.48 ug/g $\pm$ 0.06 ug/g WW for agalfish, with recoveries of 105 percent and 102 percent respectively.

The mean recovery of mercury concentrations from spiked samples was 110 percent ranging from 90-117 percent which confirms that no mercury was lost during the process of digestion and analysis.

The results of the analysis over the testing period are summarised in Table 1. Results quoted are mean values for duplicate analyses. No comparative and statistical analyses of the data have been attempted due to the bias sample sizes from differ-

ent provinces. Fish from Milne Bay have the average mercury concentrations of 2.60 ug/g WW. The mercury concentration analysed for a single mud crab (*Scylla serrata*) was 0.01 ug/g WW.

DISCUSSION

Fish are an important export commodity and revenue earner for the country and also form an essential part of the basic diet for coastal living Papua New Guineans. Because of the danger from on-going mining industry, for example in Western Province and for public health reasons in general, chemical analysis was important to determine the levels in heavy metals such as mercury and its edibility of the fish. Testing of such foods as fish is necessary due to an increasing awareness by society to the dangers to human health of heavy metals, such as mercury in the diet and the potential for fish to have dangerously high levels, particularly where caught in waters associated with mining ventures (Anon. 1989).

There is no universally accepted safe level of mercury in fish for human consumption; each country has its own standard (Petr 1978/79; Kyle 1984). However, the recommended limit set by the World Health Organisation (WHO), and adopted by such countries as Australia, is 0.50 ug/g WW (Kyle and Ghani 1982). Because various countries have their own regulations concerning the safe limits of mercury, the fish which were being exported had continully been tested for mercury to meet the required levels for the country of destination. In the present study the WHO levels were exceeded only in the Milne Bay area are in mackerel, with 6/6 samples exceeding 0.50 ug/g level. Barramundi from the same area had mean levels 0.48 ug/g WW, with 3/4 exceeding the 0.50 ug/g level.

Several studies into the mercury levels of fish have been conducted in various localities of Papua New Guinea. In a survey sponsored by the then Department of Primary Industry in 1972-74, Kyle and Ghani (1982) found the total mercury concentrations ranged from 0.32-0.57 ug/g WW in 31 barramundi from Lake Murray, Kaweto and Fly estuary of Western Province was in the excess of the World Health Organisation (WHO) recommended limit of 0.5 ug/g WW (Kyle and Ghani 1982).

Lamb (1977) found mercury levels of 0.026-0.18 ug/g WW in nine species of fish sampled from OK Tedi and Upper Fly River area, with one barramundi from Lake Murray having 0.494 ug/g WW (Lamb 1977). Reynolds and Price (1974) reported total mercury levels in some 214 samples of barramundi from Lake Murray, lower reaches of the Fly River and coastal waters around Daru contained high mercury levels, whereas low mercury concentrations were seen in fish from Baimuru and Kikori waters, Gulf Province. Kyle and Ghani (1984/85) also found that the total mercury concentrations vary with location from Gulf of Papua.

The present data collected between 1986 and 1989 show that the mean total mercury levels of fish (barramundi) from Western province were below the WHO recommended limit but the limit was exceeded in individual fish (Table 1).

None of the four species of fish (barramundi, jewfish or croakers, threadfins salmon and mackerel) from Gulf Province exceeded the WHO recommended level; the maximum level in an individual fish (barramundi) was 0.29 ug/g WW. Mercury levels of barramundi and of unidentified fish tested from Central and Bougainville Provinces likewise were below 0.50 ug/g WW and, as in Gulf Province, the fish with the highest levels were barramundi.

The highest levels of mercury recorded in the present data were in fish from Mullins Harbour, Milne Bay Province. A mean of 0.48 ug/ g WW was found in barramundi, while mackerel tested from this locality had mercury levels ranged from 1.81-3.59 ug/g WW and mean concentration is 2.60 ug/ g WW which is not safe for human consumption. there is no mining activity in the area so it has to be assumed that the fish acquired the mercury from non anthropogenic sources. These findings warrant investigations to determine the source of the mercury in the Mullins Harbour area.

As barramundi (and mackerel) are migratory fish it is possible that mercury was acquired from a locality other than Mullins Habour. Another factor to consider is that mercury accumulates in the bodies of fish over time; the levels of mercury in a fish can therefore be linked to age. It needs to be ascertained if barramundi for example, are caught at an older age than most other edible fish and whether mackerel of any age have high mercury levels in the Mullins Harbour area (Petr 1978/79; Larnb 1977; Kyle and Ghani 1981).

Although the only mud crab (*Scylla serrata*) tested had low level of mercury there is a need to investigate and determine the mercury levels of such

Table 1. **Total mercury concentration in various types of fish from provinces indicated.**

PROVINCE	TYPE OF FISH	NO. OF SPECIMEN	MERCURY CONCENTRATION MEAN, ug/g WW	MERCURY CONCENTRATION RANGE, ug/g WW*
WESTERN	BARRAMUNDI	80	0.25	(0.02 - 1.00)
	(*L. calcarifer*)	(75)	(0.21)	(0.02 - 0.43)
		(5)	(0.54)	(0.51 - 1.00)
GULF	BARRAMUNDI	56	0.11	0.02 - 0.29
	JEW FISH OR CROAKERS (Sciaenidae)	36	0.08	0.01 - 0.12
	THREADFINS SALMON (Polynemidae)	34	0.04	0.01-0.10
	MACKEREL (Scombridae)	4	0.06	0.05 - 0.07
CENTRAL	BARRAMUNDI	3	0.33	0.27 - 0.41
	WHOLE FISH (sp. unidentified)	2	0.10	0.02 - 0.17
MILNE BAY	BARRAMUNDI	4	0.48	0.36 - 0.56
	MACKEREL	6	2.60	1.81 - 3.59
NORTH SOLOMONS	WHOLE FISH	3	0.05	0.02 - 0.07

* WW - wet weight

marine bottom dwelling crustacea as crabs, prawns and crayfish as they, also, are important export commodities and form an important part of the diet of coastal people of Papua New Guinea.

The average concentrations of mercury analysed in barramundi, jewfish or croakers and threadfisn salmon over the testing period between 1986-1989 (Table 1) were close to the limit of 0.50 ug/g WW set by the Australian Government and WHO. The mackerel from Mullins Harbour, Milne Bay have very high mercury levels.

Mercury concentrations of 0.02-0.2 ug/g WW may be regarded as normal for fresh water fish from waters that are not polluted with mercury (Lamb 1977). The total mercury levels in the Western Province ranged from 0.02-1.00 ug/g WW. Thirty three percent of the samples' mercury concentrations were < 0.20 ug/g WW. Forty five of 80 barramundi samples from Western Province had mercury concentrations ranging from 0.20-1.00 ug/g WW and 9 samples were between 0.51-1.00 ug/g WW.

This confirms the previous findings by various authors (Reynold and Price 1974; Petr 1978/79; Kyle and Ghani 1984/85) that the mercury levels in fish, especially barramundi from Western Province are excessively high. Though the sample size

between Western and Gulf Provinces differ by 24 samples the indication of the differences in the mean mercury concentrations of 0.25 ug/g WW and 0.11 ug/g WW is highlighted respectively.

On whole barramundi from Lake Murray, was found to have mean mercury concentration of 0.10 ug/g WW, though below the 0.50 ug/g WW limit the barramundi could be in its growth stage, according to the various authors' findings (Petr 1978/79; Lamb 1977; Kyle and Ghani 1981). The 36 jewfish or croakers and the 34 threadfish salmon specimens analysed from the Gulf Province for the total mercury concentrations showed in the range of 0.01-0.12 ug/g WW and 0.01-0.10 ug/g WW respectively. The fish were safe for human consumption because the levels were well below the WHO recommended value of 0.50 ug/g WW.

The results from other provinces cannot be compared due to the bias sample sizes. However the Barramundi samples from Yule island, Central and Mullins Harbour, Milne Bay Provinces show elevation in the mercury concentrations, which require investigation of the mercury sources in this area. The mackerel samples from Mullins Harbour in Milne Bay province showed excessively high mercury levels. A thorough study is required to investigate the cause of considerable high level of mercury in Mullins Harbour, Milne Bay Province. Three samples of whole fish (sp. unidentified) from Take village in the Kieta area of North Solomons Province were submitted for mercury test and the analysis showed that the mercury levels ranged from 0.02-0.07 ug/g WW.

CONCLUSION

The mercury concentrations in some of the barramundi fish (*Lates calcarifer*) in Western Province were higher than barramundi fish from Gulf Province. The fish from Milne Bay Province had levels of mercury, which exceeded the WHO recommended limit of 0.50 ug/g WW. Further investigations are needed to determine the cause of elevated mercury concentration in the fish from this Province. None of the 135 fish sampled from Gulf or Central Provinces exceeded the WHO recommended mercury concentration of 0.50 ug/g WW. In Western Province, 6 percent of barramundi sampled, exceeded this concentration.

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