

Relation between Mercury Concentration and Size in the Mako Shark

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Many countries have set maximum permissible concentrations for mercury in fish which are intended for human consumption, most of these being in the range 0.5-1.0 µg/g mercury in wet tissue (HANCOCK et al. 1977). The relevance of such limits to the South African fishing industry is that mercury concentrations in fish must be lower than the maximum permissible level set by that country to which the fish are to be exported. In the event that mercury concentrations are subsequently found to be greater than the recommended level, the entire consignment may be condemned (HANCOCK et al. 1977), possibly incurring considerable financial loss to the exporter.

Shark exports from the Republic of South Africa gross approximately R 1.5 million per annum in foreign currency and, as such, represent a small but lucrative proportion of fish sales. The mako shark comprises the major portion of the total shark export, the slightly pink flesh of this species being favoured by the European consumer. The aim of the present study was to determine mercury levels in this commercially valuable species and to examine the relationship between concentration and size of an individual. At the same time the opportunity was taken to compare the results obtained from the different analytical methods in use at the two laboratories participating in this ongoing programme to determine metal concentrations in sharks.

MATERIALS AND METHODS

The mako shark *Isurus oxyrinchus* Rafinesque 1810 has been recorded from all the major oceans where it is primarily an inhabitant of the temperate and warm temperate waters (BASS et al. 1975). It is found along the coasts of southern Africa from southern Mozambique to the south-western Cape, specimens being taken in deep waters off the continental shelf and also by anglers from the shore (POPLE 1980). Although widely distributed, *I. oxyrinchus* is not locally abundant, comprising only about one per cent of the catches made by the staff of the Natal Anti-Shark Measures Board (POPLE 1980). Adult mako shark can exceed 3 m in length and are acknowledged as voracious predators (BASS et al. 1975, SMITH 1965). Their diet consists largely of fish including both elasmobranchs and teleosts (BASS et al. 1975, POPL 1980).

Sampling

Nineteen specimens of mako shark, caught by various fishing vessels off the Natal coast during the period January to March 1980, were sampled for this study of the relationship between mercury concentration and length or mass of shark. In view of the fact that the heads and tails had been removed prior to sampling, it was only possible to measure the partial length of each individual (Figure 1). However, both the standard and total lengths can be calculated, the partial length representing approximately 59.3% and 83.2% of the total and standard lengths respectively for this species (BASS et al. 1975). In addition, it was only possible to record partial mass because the specimens had been gutted at sea. Partial lengths were in the range 0.9 - 2.15 m and partial masses ranged between 15.5 and 155 kg for the individuals sampled during the present study.

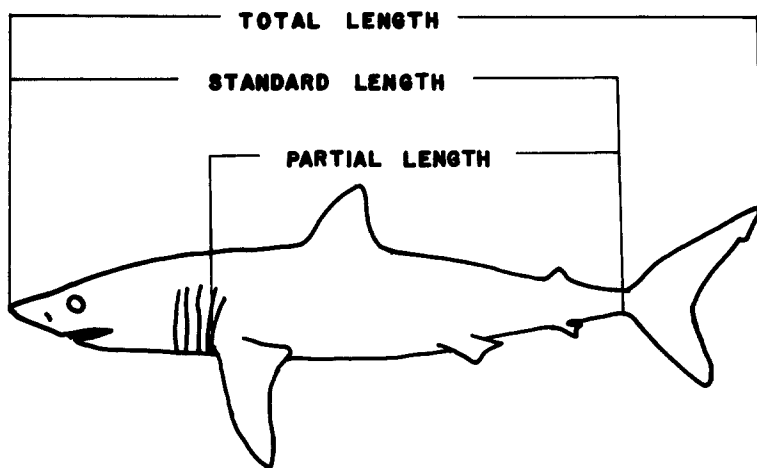


Figure 1. Relationships between total, standard and partial length in Isurus oxyrinchus.

Samples of approximately 500 g wet flesh were separated from the area adjacent to the tail stump, sealed in polythene bags and frozen to -20°C to await analysis.

Tissue Oxidation and Analysis

The determination of mercury in biological material has always proved problematical because of the difficulty of completely oxidizing the matrix while quantitatively retaining the mercury. As a considerable amount of tissue was available for this study, two oxidation methods were tested.

Many wet oxidation methods have been developed to oxidize biological material prior to mercury analysis. TEENY (1975) describes a number of these, all of which are based on the use of various mixtures of oxidizing acids, hydrogen peroxide and potassium permanganate. These methods suffer from the disadvantage of needing a trained analyst in constant attendance in order to ensure that the reaction temperature is sufficiently high to oxidize the organic material but too low to cause mercury volatilization, that the reaction is not proceeding too fast and that the organic material present has been oxidized completely.

In the present study 2-3 g of thawed wet tissue were weighed accurately into a 150-ml Erlenmeyer flask. 1 ml of concentrated sulphuric acid was pipetted directly onto the sample surface, a bubble stopper placed in the mouth of the flask and the mixture heated at 55°C for 2 h. Then 25 ml of concentrated sulphuric acid and 20 ml of a 6% mass/v potassium permanganate solution were added to the flask and the mixture heated for a further 4 h. Finally, the digestion flask was stoppered and this solution retained for analysis.

In the second oxidation method tested, the samples are mixed with an inert matrix and burned in a stream of oxygen inside a combustion tube. The exhaust gases are passed through acidified potassium permanganate to remove entrained mercury (WATLING 1978). Oxidation is complete after 5 min and the absorbing solution is free of organic substances which could affect the subsequent mercury determination. More than 50 samples can be oxidized per man day using a single combustion tube.

For the present study, 0.5 g of thawed tissue was mixed with 3 g of mercury-free sand contained in a porcelain boat. The boat was inserted into a silica tube inside a tube furnace preheated to 800°C and oxygen passed over the sample at the rate of 600 ml/min. The combustion gases were passed through a mixture of 25 ml of 5% mass/v potassium permanganate and 50 ml of 14% v/v sulphuric acid in a Dreschel bottle. This solution was stored in a stoppered vial and retained for analysis.

The mercury in these solutions was analysed by the cold vapour atomic absorption technique (HATCH and OTT 1968) after preconcentration by amalgamation with silver (WATLING 1978).

RESULTS AND DISCUSSION

Tissue Oxidation

Mercury concentrations in the nineteen samples prepared using both wet oxidation and thermal oxidation methods are presented in Table 1. Results between methods were within about 8% relative over the concentration range tested (0.55 - 5.67 µg/g mercury) and consequently mean values were used for the investigation of the relationship between mercury concentration and shark size.

TABLE 1

Mercury concentrations in wet flesh of mako shark: Comparison of results obtained following different tissue oxidation methods

Specimen No.	Acid-Permanganate, $\mu\text{g/g Hg}$	Thermal, $\mu\text{g/g Hg}$	Mean, $\mu\text{g/g Hg}$
1	1.83	1.98	1.91
2	1.79	1.51	1.65
3	1.22	1.25	1.24
4	0.55	0.63	0.59
5	3.21	3.92	3.57
6	0.73	0.71	0.72
7	0.95	1.00	0.98
8	2.91	3.08	2.99
9	2.89	2.74	2.82
10	1.15	1.13	1.14
11	1.72	1.53	1.62
12	2.44	2.39	2.42
13	3.30	3.46	3.38
14	1.79	1.75	1.77
15	2.80	2.81	2.80
16	2.19	2.33	2.26
17	0.59	0.67	0.63
18	5.49	5.67	5.58
19	1.99	2.22	2.11

In addition, prior to the analysis of the shark samples, an interlaboratory calibration exercise was carried out using a single fish sample. A result $1.98 \pm 4\%$ $\mu\text{g/g}$ mercury for six duplicate samples was achieved using the wet oxidation method, while $2.05 \pm 9\%$ $\mu\text{g/g}$ mercury was recorded following thermal oxidation of eighteen portions of the same fish sample. The thermal oxidation technique has also been used for the determination of mercury in a number of samples distributed by the International Atomic Energy Agency and absolute mercury recoveries have been checked with reference to methyl and ethyl mercuric chloride standards and standards prepared using inorganic mercury salts (WATLING 1978).

Mercury Concentration and Shark Size

The relationships between mass, length and mercury concentration in muscle tissue are presented in Figure 2. The relationships between increasing partial length (Figure 2A) and estimated total length (Figure 2B) with mercury concentration are excellent, the correlation coefficients being 0.925 and 0.932 respectively. This implies that approximately 85% of the variation in mercury concentration can be attributed to differing shark length. The

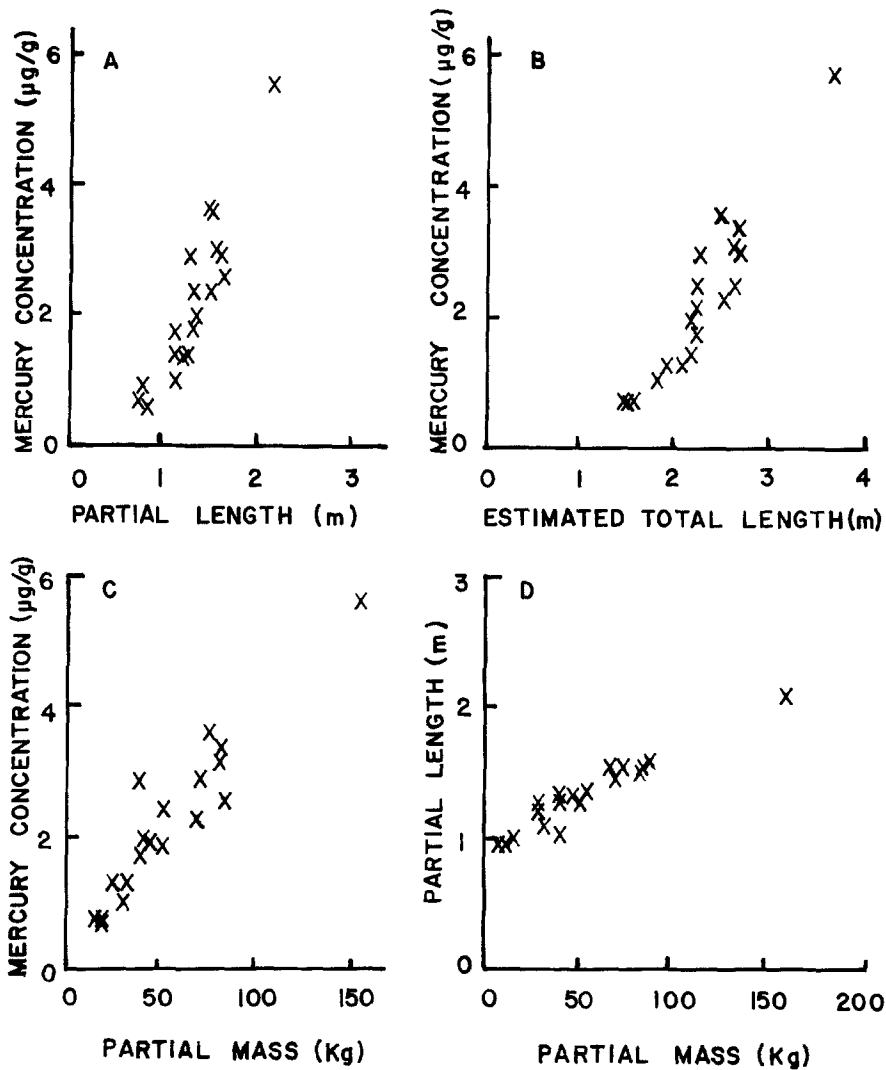


Figure 2. Relationships between mercury concentration and partial length (A), estimated total length (B) and partial mass (C), and between partial length and partial mass (D) for *Isurus oxyrinchus*.

relationship between partial mass and mercury concentration (Figure 2C), with a correlation coefficient of 0.934, indicates a similar dependence of mercury concentration on shark mass. The regression lines for these three relationships are somewhat different in that those for concentration / length do not pass through the origin while that for concentration / mass does. The reason for this can be seen from Figure 2D where there is evidence of an initial swift increase in shark length without the corresponding increase in mass which occurs later in life. The data presented in Figure 2C indicate a direct relationship between increasing mercury content and increasing shark mass. This implies that there is a slow but steady accumulation of mercury in shark tissue but does not imply the ingestion of contaminated food or the presence of mercury pollution in the shark's habitat.

These well defined relationships between concentration of mercury and shark length or mass can be of importance to the fishing industry. For example, studies on the school shark Galeorhinus australis Macleay showed that mercury levels were such that a high proportion of the larger sharks contravened the Victorian (Australia) statutory maximum level of 0.5 $\mu\text{g/g}$. By making use of the characteristic of mercury levels to rise with increasing length, legislative action was taken to the effect that the possession of school shark of length exceeding 0.77 m partial length or the equivalent 1.12 m total length is prohibited in Victoria or Victorian waters (WALKER 1976).

Whether such maximum permissible levels have been chosen as the result of careful scientific investigations or have been set arbitrarily, they nevertheless exist and are applied in many of the countries to which South Africa exports shark. The results of the present study indicate that mako shark caught off the Natal coast and with a total length in excess of 2 m, will probably contain mercury in excess of the often recommended maximum permissible limit of 1 $\mu\text{g/g}$ (HANCOCK et al. 1977). This has certain implications for both the buyer and seller of shark meat intended for human consumption. Firstly, the buyer, when testing a cargo of this species, should select the larger individuals for mercury analysis, or alternatively, should only purchase mako shark with a partial length smaller than about 1.1 m, unless the flesh has undergone some pretreatment which would reduce the mercury content. On the other hand, the fisherman who is aware that mako shark longer than 2 m are very likely to contain unacceptably high mercury concentrations and may not be saleable, could reject these individuals on site.

The South African offshore coastal environment is generally unpolluted with respect to toxic metals and, with the exception of local inputs such as Cape Town, Port Elizabeth and Durban, the nearshore environment is similarly unpolluted (CLOETE 1979). Consequently, the metal levels in local fish species are those which the fish would accumulate under natural conditions. We have, therefore, a unique opportunity in an industrialized world to study normal metal levels in commercial fish. Continuing

research is being undertaken at our two laboratories, in collaboration with the Natal Anti-Shark Measures Board, to determine metal levels in South African fish, with particular reference to mercury.

If mercury accumulation is as well defined for local fish species as has been shown for mako shark, it must be assumed that these apparently high concentrations are normal and that man has lived with this situation for many years. Therefore, further detailed studies of the natural levels of metals in fish and other seafood, complemented by thorough investigations of human dietary habits, must be carried out in order to avoid the establishment of unrealistic 'permissible' levels of metals in such food.

ACKNOWLEDGEMENTS

The authors wish to thank Mrs B Davis, Director of the Natal Anti-Shark Measures Board, Durban, for her enthusiastic support of this collaborative research programme. This research was carried out as part of the South African National Programme for Environmental Sciences (Marine Pollution Section). The financial and administrative assistance of the Department of Water Affairs, Forestry and Environmental Conservation and the Cooperative Scientific Programmes Unit of the CSIR are gratefully acknowledged.

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