

LEAD ACCUMULATION BY HAMMERHEAD SHARK, *SPHYRNA COUARDI* (C). OFF LAGOS COAST, NIGERIA.

BY

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ABSTRACT

Levels of concentration of lead in the hammerhead shark, *Sphyrna couardi* (c) off the Lagos Coast were investigate. The standard length of the specimens examined ranged from 31.4cm to 47.2cm, while the weights ranged from 451.5 to 1,667g. The lead concentration ranged from 0.11ugG to 0.38ugG. The mean lead concentration was 0.56ugG (dry weight). The gill has the highest lead concentration. There was no linear correlation between the length and weight and the amount of lead concentrated.

INTRODUCTION

Heavy metals are regarded as an important source of pollution, not just because they are toxic at relatively low concentration, but also because they are not subject to degradation hence upon introduction they become permanent addition into the environment. The uptake and storage of these metals by aquatic organisms when exposed repeatedly to sublethal concentration of these toxins also leads to the organism's tissue concentration of heavy metals to become several orders of magnitude higher than that of control animals, a phenomenon known as bioaccumulation. This increase in the tissue's metal concentration occurs as a result of the net gain in metal concentration due to the low excretion rates of the metals from the animals body and the subsequent induction of metal detoxification systems such as the formation of metal granules and synthesis of low-molecular-weight-protein e.g. metallothionien (Bryan and Langston, 1992).

Lead is an environmental pollutant known to cause damage to human health, affecting specially the central nervous system, reproductive organs, the immune system and kidney (Villagra *et al* 1997). It is regarded as a cumulative poison to mammals, symptomatically, acute lead poisoning usually affects the gastrointestinal tract or the nervous system and occasionally it affects both. There can be a sweetish metallic taste, burning in the mouth, severe anorexia, nausea, severe headache and vomiting. For these and other symptoms, scientists developed interest in studying the toxicity of the metal.

From the perspective of reproduction, lead affects both men and women. Reported effects in women include infertility, miscarriage, pre-eclampsia, pregnancy hypertension and premature delivery (Winder, 1993). Lead may induce imprinting mechanism (Tchernitchin & Tchernitchin, 1992), causing persistent changes in uterine estrogen receptors (Wiebe and Barr, 1988) and overy LH receptors (Wiebe *et al* 1988) following perinatal exposure.

In *Mytilus edulis* (a mollusc), studies on the uptake of lead showed that the kidneys contained 50-70% of the total lead and were the tissues which gained and lost it most readily. (Schulz-Baldes, 1974).

Ireland and Wootton (1977) reported that in both *Littorina and Thais*, the concentration of lead in the shell was far higher than the concentration in the soft body; they further mentioned that in both species the lead content of the shell accounted for about 80% of the total lead content.

While the lead value reported by Segar *et al* (1971) was slightly higher in *Patella* shell than ody, but it was not possible for them to know whether it was significantly different since no comparison was made between body and lead values. Lead was also found in the tissues of various mammalian species to be concentrated in the bone (Blaxter, 1950; Schroeder and Tipton, 1968, Smith *et al* 1970; Mierau and Favara, 1975; Welch and Dick, 1975).

Robert *et al* (1978) on their investigation on the acute toxicity and bioaccumulation of lead and cadmium in aquatic invertebrates reported that lead was acutely toxic to amphipods and caused greater than 50% mortality at concentrations of $136 \mu\text{g l}^{-1}$ and above after 4 days of exposure. They further reported that lead exposures with stoneflies, caddiesflies and snails suggested tha tsome aquatic invertebrates were relatively insensitive to this metal, even after 28 days exposure.

Merlini *et al* (1977) investigated the accumulation of lead by an edible freshwater fish aat pH 7.5 and pH 6.0; according to their investigation, they found out that t the lower pH the sunfish concentrated almost three times more lead than at the higher pH. They also concluded that when lead was added to Lake Maggiore water as a salt only 8% remained in the ionic state and as such was picked up by fish; this they said showed that lead accumulation by fish would depend on its chemicophysical state, which in turn, depend on the water quality of the aquatic environment.

Mathis and Kevern (1975) stated that the element was quite toxic to aquatic organisms; with fish being the most sensitive group. They found that the hybrid sunfish in Wintergreen Lake had a mean of 0.98 ± 0.110 ppm of lead whilst carnivorous fish from the Illinoids River were reported to have 0.57ppm (Mathis and Cumming, 1973).

Patrick *et al* (1979) compared the concentration of lead in plankton samples from Ulliswater with concentrations in samples from Bassenthwaite Lake and Mockerkin Tarn. They found out that *Melosira and Asterionella* blooms from ullswater contained up to $772 \mu\text{gPbg}^{-1}$ organic dry weight, whilst samples from the other lakes contained 29-169 μgpbg^{-1} , and that the algal blooms contributed 1-2mg Pbm^{-2} to the sediment.

Fergusson *et al* (1981) examined lead in human hair and found the mean lead content of the headhair of 203 citizens of Christchurch, New Zealand to be $10.4 \mu\text{gg}^{-1}$ while the mean level for 16 employees of a local battery factory was $363 \mu\text{gg}^{-1}$ and that of 65 members of employees families was $67 \mu\text{gg}^{-1}$. They further reported that the high mean for the family members (both adults and children) was significantly different ($P < 0.001$) from the mean for the city survey, which revealed a problem arising from employees transferring lead dust home, probably in their working clothes.

Simpson and Hunt (1979) showed lead poisoning due to the ingestion of lead fishing shot as the cause of death of a number of mute swans (*Cygnus olor*gmelin. They reported that the area in which they were feeding was heavily contaminated with fishing shot. They further reported that the kidneys of the dead birds contained from 350 to 6650 μgg^{-1} DM of lead and blood lead levels in the remainder of the bird were greatly elevated, rising to 3290 $\mu\text{g}/100\text{ml}$.

According to Joosse *et al* (1979) high lead concentrations in the food of litter-dwelling *Collembola* appeared not to have any harmful effects, and that most of the lead remained unabsorbed and was concentrated in the faeces, while of the absorbed lead 30% was stored in intestinal epithelium cells and excreted by periodic renovation of the intestinal epithelium, which occurred at each moulting.

Atomic absorption spectrophotometric analysis was conducted by Braham 91973) on tissues samples taken from 19 organs in the California sealion, *Zalophus californianus* to determine the distribution and concentration of the heavy lead metal. He found out that lead was accumulated in significantly higher concentrations in hard tissues, bone and teeth, than in soft tissue such as fat and muscle.

The hammerhead shark, *Sphyrna couardi* belongs to the family sphyrnidae. Members of the family are widely distributed in all oceans. They are swift and powerful. They are carnivores. Some species are fished for leather and oil which in one of the natural source of vitamin A and to a lesser extent of vitamins C and D (Chandry, 1970).

In Nigeria, especially in the coastal and riverine areas sharks are cherished as food. But there was press controversy (The Guardian, 3 July 1985) on the concentration of heavy metal especially mercury, lead and cadmium in sharks, hence the need for this investigation.

Specific objectives of this study was to evaluate the lead concentration in various organs of the hammerhead shark and relates level of concentrations to the lengths and weights of the specimens.

MATERIALS AND METHODS

Sampling

Samples of *S. couardi* were collected over the period November 1986 and January 1987 from off Lagos Coast, Nigeria. The vessel MV. Massey was used to collect the specimens. The vessel was 13.0cm long with 125 Horsepower caterpillar engine. Samples were caught by trawling using beam trawl with cord end 2 inches (5.08cm) and wing or belly of 3 inches (7.62cm). They were preserved with ice blocks while at sea and in a deep freezer prior to laboratory analysis.

Sex, weight (to the nearest tenth of a gram) and standard length (in centimetres) of each specimen were recorded. A total of 17 specimens were examined for this study.

Drying Method

Samples of different organs of the fish were put in clean glass petri dishes with identification tags. For the skin, portion of the fish was boiled with distilled water in a glass container, and then the skin was carefully removed.

The glass petri dishes with the organs were placed in the oven at 100°C till they were dried to constant weights.

Dried weight of samples were placed in a dessicator, later they were grinded into powdered form in a glass mortar. The powdered form of each organ was properly mixed and divided into four portions, one of the portion was taken and divided again into four portions. Some grams of these portions were taken and used for acid digestion.

Digestion Method

The various organs used and the quantities used for digestion were as follows:

- (a) 2g of gills and 50ml of analar Conc. HNO₃.
- (b) 2g of guts and contents and 50ml analar Conc. HNO₃.
- (c) 2g of tissue (muscle) and 50ml of analar Conc. HNO₃.
- (d) 2g of skin and 50ml of analar Conc. HNO₃.
- (e) 2g of gonad and 50ml of analar Conc. HNO₃.
- (f) 2g of kidney and 50ml analar Conc. HNO₃.
- (g) 2g of wet sample of liver and 50ml of analar Conc. HNO₃.

Wet sample of liver was used because it was impossible to dry the organ.

Each of the known weight powdered organ was placed in a 100ml glass conical flask and 50ml of analar concentrated HNO₃ added in a fume cupboard. A clean glass-filter funnel was used to cover each flask in order to promote refluxing of the acid. The flasks and contents were left overnight in order to allow digestion at room temperature.

Each flask together with its content was then placed on a hot plate in the fume cupboard and digestion was carried out at 40°C until near boiling after which the flasks were then allowed to cool.

The volume of the cool digested samples were made up to 100ml with distilled water in clean volumetric glass flasks.

The digested samples were then filtered with a watchman filter paper and each sample solution was stored in a clean plastic container and then kept for lead analysis.

Determination of lead in samples using Atomic Absorption Spectrophotometer (AAS)

The procedure involved the construction of a calibration curve for lead using standard solutions containing known weight of lead.

Preparation of Calibration Curve

A series of standard solutions containing 0.2, 0.4, 1.0, 2.0 $\mu\text{gPb}^{2+}/\text{mL}$ were prepared from the stock solution which contained $1,000 \text{ mg l}^{-1}$. Each standard solution was run through a PYE UNICAM SP9 AAS with acetylene gas and compressed air. The absorbance of each solution was read at a wavelength (λ) of 217.0 nm and a maximum current of 6 mA.

A graph of concentration in $\mu\text{gPb}/\text{mL}$ of solution against its corresponding absorbance was plotted.

Determination of lead in samples

Each digested sample was run through the AAS. The absorbance for each sample was read and recorded at the same wavelength for the standard solution. The equivalent lead concentration for each absorbance reading was determined from the calibration curve by extrapolation.

Results

Construction of a calibration curve for lead:

Fig 2. Shows the result obtained for the standard curve preparation for the determination of lead in *S. couardi*. The result shows a linear relationship between absorbance and the concentration of lead used.

Percentage composition of lead in different organs of *S. couardi*.

The organs examined for lead concentration were the gills, gonads, guts and their contents, kidneys, livers, muscles and skins.

Table 1 shows the different organs, lead concentration range, mean and percentage lead composition in these organs. Figure 3 shows the percentage composition of lead in these organs. The result shows that the gill has the highest percentage lead composition.

Relationships between length or weight and lead concentration in different organs

Table 2 and 3 show the length or weight ranges, lead concentration in the different organs, the regression constants, regression coefficient, as well as the correlation coefficient respectively.

Discussion

The result obtained for the construction of lead calibration curves showed linear relationship between absorbance and the concentration of lead used. This was in agreement with Lambert and Beer's Law (1952) cited by Fodeke (1980) which stated that the degree of absorption of light depended on thickness of the layer transversed and on the molecular concentration only.

S. couardi had a mean of $0.56 \mu\text{gpb}^{2+}\text{G}^{-1}$ (dry weight) which was higher than that reported by Mathis *et al* (1975) in the hybrid sunfish in Wintergreen Lake that had a mean of $0.198 + 0.110\mu\text{gG}^{-1}$ of lead and almost equal to that of carnivorous fish from Illinois River reported to have $0.57 \mu\text{gG}^{-1}$ (Mathis and Cumming, 1973). The highest percentage lead composition was found in the gill, which was one of the organs, accepted to be the passage for heavy metals. Studies on the uptake of lead in *Mytilus edulis* (a mollusc) by Schulz-Baldes (1974), however showed that the kidneys contained 50-70% of the total lead and were the organs which gained and lost it most readily.

No significant linear relationships were obtained between the lead concentration in the different organs and length (or weight). Mathis *et al.* (1975) also reported that lead could not be correlated with length or weight in five fish species studied. The correlation coefficients (r) obtained for concentration of lead in gill and gonad against length were very low and negative (~ -0.1). While that obtained for the gut and its content showed a significant positive correlation with the length, (or weight) one explanation for this might be due to the feeding nature of this species. They are known to be carnivores, hence small *S. couardi* will feed on small animals and their low lead

content as compared to larger ones. The values obtained for kidney and liver showed high negative correlation, the reason might be due to the fact that the lead in most of these organs were just below the detection limits of the analytical equipment.

No significant correlation was found between the muscles that contained lead the lengths (or weight). A low positive correlation trend was found between concentration of lead in skin and length (or weight).

This study has shown that lead is bioaccumulating in the organs of *S. couardi* off Lagos coast, Nigeria, although is very low concentration.

The specimens for this study were obtained off Lagos Coast. Lagos is an urban city with many motor vehicles and industries discharging most of their effluents into the Lagos Lagoon which opens into the sea via the Lagos harbour. Apart from industrial effluents, there is also the problem of sewage pollution which eventually gets into the sea. Cement works, fruit and vegetable canning; grain milling, rubber processing, saw milling, steel and tanning are some of the industries, whose effluents are common to the area where the specimens were collected. These industrial effluents and sewage discharge would definitely be the major source of this heavy metal (lead) in the area of collection.

Apart from the above, release of metals especially lead in exhaust fumes of motor vehicles and machines used in various industries mentioned above could also be washed off and discharged into the sea.

The shark is a favourite diet of inhabitants of coastal areas in Nigeria. To reduce the level of this metal in the diet, it might tentatively be suggested that for the shark to be eaten, the gill, gut and its contents, kidney, liver and skin be removed before consumption. Shark should also form a minor part of the diet.

The liver of this shark which is known to be rich in vitamins C and D concentrated the least lead, hence should be no threat for the production of shark liver oil.

As an alternative it is suggested that shark be given up as food fish completely and used only as fish meal.

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Table 1: Range, Mean and Percentage Composition of lead in different organs of *S. couardi* (Combined sexes).

{PRIVATE }Organ	Range (UgG ⁻¹)	Mean (UgG ⁻¹)	Percentage
Gill	0.11-0.38	0.1071	19.12
Gonad	0.11-0.30	0.0865	15.44
Gut	0.15-0.34	0.0894	15.97
Kidney	0.15-0.38	0.0535	9.56
Liver	0.16-0.27	0.0253	4.52
Muscle	0.15-0.30	0.1047	18.70
Skin	0.15-0.30	0.0935	16.70

Table 2: Relationship between length and lead concentration in different organs.

{PRIVATE }Organ s	Standard length ranges (cm)	Lead concentration (UgG ⁻¹)	Regression constant (a)	Regression coefficient (b)	Number of species (n)	Correlation coefficient (r)
Gills	32.2-47.2	0.11-0.38	0.2728	-1.1071x10 ⁻³	9	-0.0986
Gonad	31.4-47.2	0.11-0.30	0.2692	-1.5104x10 ⁻³	7	-0.1244
Gut	31.4-47.2	0.15-0.34	-0.2367	1.1572x10 ⁻²	7	0.8556
Kidney	31.4-47.2	0.15-0.38	0.5781	-9.5909x10 ⁻³	4	-0.6501
liver	31.4-43.6	0.16-0.27	0.5531	-9.0164x10 ⁻³	2	-1.0042
Muscle	32.0-43.6	0.15-0.30	0.2601	-9.5665x10 ⁻⁴	8	-0.0918
Skin	32.2-43.9	0.15-0.30	-0.0538	6.3722x10 ⁻³	8	0.4249

Table 3: Relationship between weight and lead concentration in different organs

{PRIVATE }Organ s	Standard length ranges (cm)	Lead concentration (UgG ⁻¹)	Regression constant (a)	Regression coefficient (b)	Number of species (n)	Correlation coefficient (r)
Gills	562.9-1,667.6	0.11-0.38	0.2023	-9.4x10 ⁻⁸	9	-0.3937x10 ⁻³
Gonad	495.7-1,667.6	0.11-0.30	0.2357	-2.2816x10 ⁻⁵	7	-0.1484
Gut	495.7-1,667.6	0.15-0.34	0.0573	0.1441x10 ⁻³	7	0.8602
Kidney	451.5-1,667.6	0.15-0.38	0.3313	-1.2107x10 ⁻⁴	4	-0.6294
liver	495.7-1,503.4	0.16-0.27	0.3241	-1/0916x10 ⁻⁴	2	-1.0042
Muscle	562.9-1,667.6	0.15-0.30	0.2331	-0.9656x10 ⁻⁵	8	-0.0730
Skin	562.9-1,531.3	0.15-0.30	0.0995	8.5536x10 ⁻⁵	8	0.4892