# Trace Metals in Fish and Shellfish

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Finfish and shellfish accumulate chemicals from the polluted environments. The chemical residues of concern are certain heavy metals, polychlorinated biphenyls (PCBS) and other pesticides. Their abnormal levels in seafoods pose hazards to public health. Improvement of environmental quality alone can provide safe fish. Background levels of trace metals in seawater and freshwater the world over are given in Annexure I.

Toxic metals above the normal level impair the quality, safety and market potential of seafoods. The elements of most concern are cadmium, mercury, lead, arsenic etc. Human poisoning by mercury in seafoods was well documented after the mass poisoning episode in the Minamata bay area of Japan. On the basis of surveys carried out on pollution, a number of Governments have given advice to the public and industry on the safety of fish. The regulatory and health authorities of many countries have introduced permissible limits for metals in seafoods.

## Mercury in aquatic organisms

When exposed to mercury containing diet or water, fish, shellfish etc. gradually accumulate the metal throughout their life. Food chain enrichment of mercury is taking place in the aquatic environment. Eventually, man consuming the fish inevitably suffers from the results of this enrichment taking place at each trophic level ie. where less is excreted than ingested. However, analysis of fish flesh in Sweden, Finland, U.S.A., Canada, U.K., Japan and elsewhere have revealed that mercury content of marine fish, does not, for the most part, exceed a value of 0.5 ppm.

In general, the level of Hg in marine fish from unpolluted areas is in the range of 0.01-0.3 ppm and in fish from polluted waters the concentration goes up to 2.5 ppm. However, fish caught from the polluted Minamata area had a mercury content of about 50 ppm. Black marlin from Australia contained 7.3 ppm Hg (average). Highest levels of mercury in freshwater fish were reported by Scandinavian authors. Thus, brown trout *(Salmo trutta)* from polluted area was seen to have a Hg content of 4.35 ppm against the normal value of 0.21 ppm while pike *(Esox lucius)* from Sweden contained 8 ppm Hg. Contaminated fish species from Elbe Estuary in Germany contained an average Hg conc. of 1.5 ppm.

High concentration of mercury was found in tuna and swordfish (particularly large size) collected from most parts of the world, even from unpolluted areas. However, the value remained unaltered for over a century.

| Fish | Range of value in ppm | Mean Hg ppm |
|---|---|---|
| Tuna (museum specimen) | 0.03 - 1.51 | 0.95 dry wt. basis |
| Tuna (recent sp.) | 0.44 - 1.53 | 0.91 " |
| Swordfish (recent sp.) | 0.94 - 5.08 | 3.1±1.5 " |

Most small or medium sized tuna contained levels that fall below the limit. On the other hand, many large tuna and swordfish of commercial size exceeded the limit. As a result of these findings, processed tuna and swordfish of high mercury content have been withdrawn from sale, the processing of sword fish has ceased and careful checks by the canning industry and Government agencies on the mercury content of tuna raw material have been instituted. It is observed that selenium has got antagonistic effect on mercury and that the toxicity of Hg is reduced by selenium.

### *Limits for mercury in fish*

The food regulatory and health authorities in some countries have issued prescriptions regarding the levels of mercury in seafoods. Thus, Canada fixed the max. permitted limit as 0.5 ppm, whilst the limit in the U.S.A., Japan, Sweden and Finland is 1.00 ppm. Indian standard for Hg is 0.5 ppm.

## Cadmium

Contamination of the aqueous environment with cadmium is less widespread. However, in recent years, high levels of Cd was observed in marine products from certain regions. High levels of cadmium in cephalopod molluscs have been reported from different parts of the world. About 50% of squid and cuttlefish imported into Italy and Yugoslavia had exceeded the tolerance limit for Cd (1 ppm.). High levels of cadmium (2.9 - 10 ppm) in the edible parts of squid, *Loligo patagonica* have been reported. Raw whole squid contained on an average 4.0 ppm. of cadmium.

The important sources of cadmium in the environment are waste discharges from zinc smelting, electroplating industry, pigment plants and producers of alloys and batteries. Significant amounts of Cd reach the agricultural soil from phosphatic fertilizers. Coal and oil combustion, cement production and incineration of waste products release huge quantities of Cd into the atmosphere. The normal concentration of cadmium in seawater is 0.02 µg/l. Concentration factor (CF)* of more than 4500 has been reported for some marine organisms. Concentration of Cd toxic to aquatic life is in the range of 0.01 to 0.1 ppm. High content of Cd is found in shellfish from polluted waters. Mussel from Derwent estuary (Tasmania) is highly contaminated with Cd, ranging in concentration from 6.2 to 38 ppm (dry wt); squid and cuttlefish from certain regions contain high content of Cd. The levels of cadmium and other metals in fish and shellfish caught from different parts of the world including India are presented in Annexures II & III respectively.

### Lead

Lead is another cumulative poison. Lead poisoning causes chronic kidney infection. The toxicity of lead to marine organisms is not known

*Ratio of the concentration of the metal in the body to that present in the environmental water precisely. Fish/shellfish from the Severn Estuary, England is contaminated by lead. In a few cases, particularly shellfish taken from inshore waters, the organisms were found to contain high levels of lead. Mussels taken from the Derwent Estuary (Tasmania) were found to be unfit for human consumption because of their high metal content (Hg, Zn, Cd & Pb). Lead content varies from 16-532 ppm (dry wt) in mussels from the estuary. This may cause risk to health, if contaminated fish is eaten in excess. A concentration factor upto 1400 has been reported for marine organisms. Chronic lead poisoning in humans from contaminated food or water is common. Permitted limit in canned seafood is 5 ppm.

### Other metals

The position with regard to the effect of other metals (Cu, Zn, As, Se etc.) on fish quality is not so serious in so far as analysis has not often revealed high concentrations. In a few cases, particularly shellfish taken from some inshore areas, rather high concentration of Cd, Zn and Pb are found. If eaten in conspicuously high amounts, such fish could possibly cause risk to health.

### Copper and Zinc

Higher than normal concentration of copper and zinc in shellfish like oysters result in an unpleasant metallic flavour and green colour. When the concentration of copper or zinc in water increases to about 0.01 to 0.1 ppm respectively, oysters become green in colour. They are known as 'green sick' oysters. Copper and zinc above the concentrations indicated above harm the oysters. The soft parts of green oysters contain copper and zinc in concentration as much as 100 times greater than the normal case (it takes about 2 weeks to become green). The concentration factor for marine organisms was reported to be 7500 for copper.

Copper is toxic to man in quantities of about 100 mg, but copper poisoning as a result of eating copper contaminated shellfish (or fish) is unlikely since their taste renders them unpalatable. This coppery flavour of oysters reduce their market value. Again, high content of copper in crab meat and prawns produces blackening in canned products due to the formation of CuS which again undermines the quality of the product. Permitted limit of copper in canned seafood is 10 ppm.

The toxic limit of zinc for adult fish and shellfish is of the order of 10 ppm. The concentration factor is as high as 32,500. Zinc is toxic to man only in large doses, and since high concentration imparts green colour to fish/shell fish it is somewhat unlikely that specimens contaminated to such an extent would be eaten. Levels of zinc in some bivalves and fish are given below:

| Fish/shellfish | Range (ppm) | Mean (ppm) dry wt. | Country |
|---|---|---|---|
| *Mytilus edulis* | 50 – 180 | 31 | New Zealand |
| *M. edulis* | – | 516 | Tasmania |
| -do- | 85 – 359 | 169 | Norway |
| *Crassostrea gigas* | – | 7227 | Tasmania |
| *C. glomerata* | 97 – 900 | 337 (wet wt.) | New Zealand |
| *Mugil cephalus* | – | 17 (wet wt.) | " |

Permitted level of zinc in seafood is 50 ppm.

## Arsenic

Arsenic is also a cumulative poison. Concentration factor in marine animals is as high as 3300. In areas of high As concentration, shellfish contain as much as 100 ppm. 100 mg of As may cause poisoning in man and 130 mg has proved fatal. Arsenic content along the food chain within a defined polluted area is given below:

| | |
|---|---|
| mussels | 14.1 - 16.7 ppm |
| prawns | 62.9 - 80.2 and |
| different fish species | 43.4 - 188.0 ppm |

(All data on dry weight basis).

Independent of environmental pollution, many marine organisms contain appreciable amounts of As in their tissue. It is reported that carnivorous gastropods are characterised by high levels of As (16.8 to 67.9 ppm) in tissues, especially in muscle.

The highest As content was found in American plaice (188 ppm).

## Selenium

The normal concentration in seawater is 0.4 μg/1. There is some evidence of food chain concentration at least in freshwater with high building up in the liver of fish. Large specimens of tuna and swordfish contain relatively high levels of Se. Black marlin from Australia contains 2.2 ppm of Se in the body. The element is highly toxic to man. The safe level in food is considered to be not more than 3 ppm. Selenium and its compounds cause serious injury to the kidneys, liver and heart. However, the Se/Hg antagonism does not produce much toxicity in animals.

## Chromium

An incidence of catastrophic heavy metal poisoning was reported from highly toxic Cr(Vi) contained in untreated slimes and factory wastes. The Nippon Chemical Industrial Co., in Japan deposited approximately 5,30,000 tons of unreduced slimes and wastes containing hexavalent Cr around Tokyo. During August 1975 it was found that drinking water in Tokyo collected from ground water, near the Cr (VI) containing spoil heaps, contained more than 2000 times the official threshold limit. Normal concentration in seawater is 0.08 μg/1 and in freshwater, 0.5 μg/1.

## Trace metals in Indian seafoods

The heavy metal levels in Indian seafoods were extensively studied by the author. The metal levels in various seafoods are given in Annexure III. The study indicated that toxic trace metals (except cadmium) are well below the permitted limit in almost all the marine products. The level of cadmium in cuttlefish and squid often exceeded the limit and some consignments from India were rejected by Italy and Spain in the 80s. A detailed investigation at the Central Institute of Fisheries Technology, Cochin showed that cadmium was mainly concentrated in the liver and gut of cephalopods and the edible meat does not contain levels above the limit. Accordingly, an improved processing method to reduce cadmium content was also demonstrated to the industry. The permissible limit of toxic metals in seafoods is given in Annexure IV.

Arsenic and selenium are the other two elements in cephalopod molluscs that cause concern. Higher levels of As and Se are found in squid and cuttlefish (Annexure-III). Arsenic was found to be accumulated in the liver of cuttlefish.

### *Analytical method for the determination of trace metals*

Atomic Absorption Spectrophotometric method (AAS) is probably the most widely used method for the determination of trace metals. The process involves homogenisation of edible portion of the fish (excluding bones and scales), wet digestion using con. nitric acid and sulphuric acid followed by determination of the metals by Flame Atomic Absorption Spectrophotometer. The sensitivity of the method can be increased by chelation with ammonium pyrolidine dithiocarbamate (APDC) or sodium diethyl dithiocarbamate (Na DEDC) and extracting with methyl isobutyl ketone (MIBK) after adjusting the pH. It is then aspirated over the flame in AAS.

Mercury is determined using cold vapour technique and arsenic and selenium after generation of metal hydrides. The digestion for Hg is carried out in a Bethge Apparatus using a mixture of con. $HNO_3$ and $H_2SO_4$ in the ration 4:1 (v/v). Mercury is estimated using a Mercury Analyser in the cold after reducing with stannous chloride.

## Annexure - I

*Background levels of trace metals in seawater and freshwater

| Element | Sea water µg/l | Freshwater µg/l |
|---|---|---|
| Arsenic | 2.1 | 2 |
| Cadmium | 0.01(s) - 0.07(d) | 0.07 |
| Chromium | 0.08(s) - 0.15(d) | 0.50 |
| Copper | 0.04(s) - 0.14(d) | 1.80 |
| Lead | 0.005(s) - 0.001(d) | 0.20 |
| Mercury | 0.011 | 0.01 |
| Selenium | 0.04(s) - 0.13(d) | 0.1 |
| Zinc | 0.01(s) - 0.62(d) | 10 |

* Adapted from Forstner & Wittmann (1979)

s - **Surface water**

d - Deep water

## Annexure - II

* Heavy metals in seafoods (ppm drywt. basis)

| Seafood | As | Cd | Hg | Pb | Cu | Zn | Cr | Country |
|---|---|---|---|---|---|---|---|---|
| I. Molluscs (Bivalves) | | | | | | | | |
| *Mytilus edulis* | – | 10 | – | 12 (3-25) | 9 (5-11) | 31 (50-180) | 16 (9-24) | New Zealand |
| *M. edulis* | | 2.09 (0.2-18.16) | – | – | 0.73 (0.47-1.45) | 42.7 | – | Australia |
| *M. edulis* | – | 18.6 (4.3-38) | 4.2 (0.4-13) | 199 (3-352) | – | 516 (171-1350) | – | Tasmania |
| *M. edulis* | – | 5.1 | – | 9.1 | 9.6 | 91 | 1.5 | U.K. |
| *Crassostrea virginica* | 1.3 | 3.2 | 0.47 | 0.8 | 161 | 322 | – | U.S.A. |
| *Cardium edule* | – | 1.5 | – | 0.76 | 11 | 130 | – | U.K. |
| *C. edule* | – | 0.3-0.6 | – | 0.7-2 | 6-26 | 100-200 | – | Europe |
| II. Crustaceans | | | | | | | | |
| *Crangon crangon* | – | – | 0.03-12 | – | – | – | – | F.R.G. |
| *C. crangon* | 0.6 | 0.4 | 0.02 | 0.2 | 34 | 14 | – | Texas |
| III. Fish (Marine) | | | | | | | | |
| *Scomber japonicus* | – | – | – | – | – | 7.2 | 0.65 | S. Africa |
| *Seriola grandis* | – | 0.006 | – | 0.40 | 0.58 | 9.5 | 0.02 | New Zealand |
| *Mugil cephalus* | 1.0 | 0.1 | 0.1 | – | 1.9 | 17 | – | N. Atlantic |
| Tuna (museum sp.) | – | – | 0.95 (0.53-1.51) | – | – | – | – | U.S.A. |
| Tuna (recent) | – | – | 0.91 (0.44-1.53) | – | – | – | – | U.S.A. |
| Swordfish | – | – | 3.1 | – | – | – | – | Pacific/ California |

* Adapted from Forstner & Wittmann (1979)

## Annexure - III

* Trace metal levels in the major seafood items (mg/kg wet weight, mean, range and ±S.D. (* µg/kg wet weight) of India

| Product | * Mercury | Cadmium | Lead | Copper | Zinc | Arsenic | Selenium |
|---|---|---|---|---|---|---|---|
| Cephalopod | | | | | | | |
| Cuttlefish, whole | 66.3±46 | 3.89±3.23 | 0.66±1.2 | 9.4±6.4 | 12.8±4.6 | 11.7±1.6 | 4.6±0.4 |
| | (6.6-179) | (0.07-10.96) | (0-8.1) | (1.2-35.1) | (10.1-34.2) | (9.5-13.9) | (4.2-5.0) |
| Cuttlefish, fillet | 32.9±16.5 | 0.4±0.3 | 0.71±1.2 | 1.6±1.0 | 10.7±3.5 | 10.6±3.3 | 5.01±1.1 |
| | (8.1-58.9) | (0.1-0.9) | (0-6.3) | (0.4-4.7) | (6.3-22.2) | (7.6-14.7) | (4.1-6.3) |
| Squid, whole | 54.6±21.9 | 1.6±2.3 | 0.9±0.8 | 3.5±3 | 12.2±4.8 | 3.4±1.2 | 3.9±0.4 |
| | (10.1-87.6) | (0.08-8.0) | (0-1.6) | (0.4-13.9) | (6.4-19.9) | (2.3-4.5) | (3.5-4.3) |
| Squid, tube | 45.9±25 | 0.2±0.2 | 1.1±1.2 | 2.8±2.3 | 12.1±6.7 | 2±4.5 | 3.9±0.6 |
| | (8-76.4) | (0.07-0.7) | (0.3-4.9) | (0.5-12.1) | (4.6-30.5) | (1.86-2.15) | (3.3-4.4) |
| Molluscs | | | | | | | |
| Oysters | 48.8 | – | 0.30 | 20.9 | 1166 | N.D | N.D |
| | (38-91) | | (0-0.72) | (12.4-30.7) | (786-1944) | | |
| Clams | 24.6 | 0.2 | 1.8 | 4.94 | 12.7 | N.D | N.D |
| | (11-35) | (0.1-0.34) | (0.7-2.5) | (3.1-9.8) | (8.6-19.8) | | |
| Mussel | 38.2 | 0.3 | 0.8 | 2.1 | 12.3 | N.D | N.D |
| | (23-65) | (0.2-0.6) | (0.6-1.2) | (1.37-3.86) | (8.9-16.8) | | |
| Crustaceans | | | | | | | |
| Prawns | 30.3 | – | – | 2.8 | 6.1 | – | – |
| | (21–49) | | | (1.7-4.6) | (4.1-7.8) | | |
| Lobsters | 46.4 | 0.08 | 0.23 | 3.4 | 10.4 | N.D | N.D |
| | (32-58) | (0.06-0.2) | (0-0.6) | (2.8-4.2) | (9.5-12.8) | | |
| Crab | 121 | 0.2 | 0.13 | 13.7 | 66.7 | N.D | N.D |
| | (100-370) | (0.1-0.3) | (0-0.18) | (7.6-18.3) | (59-76) | | |
| Finfish | 26 | 0.03 | – | 0.53 | 4.35 | N.D | N.D |
| | (18-43) | (0-0.07) | | (0.04-2.02) | (2.3-7.8) | | |

* Adapted from Lakshmanan (1989, 1993)

## Annexure - IV

Legal admissible limits of hazardous substances in seafood imports

| Countries | Mercury ppm | Cadmium ppm | Arsenic ppm | Lead ppm | Tin ppm |
|---|---|---|---|---|---|
| Japan | 0.4 total<br>0.3 Methyl | | | | |
| U.S.A. | 1.0 total | | | | |
| F.R.G. | 1.0 total | 0.5 | | 0.5 | |
| U.K. | 0.5 | | 1.0 | 3.0 canned seafoods<br>10.0 shellfish<br>5.0 dryfish<br>1-2 finfish | 250 |
| France | 0.5 molluscs & crustaceans<br>0.7 Tuna | 0.5 | 1.0 | | |
| Netherlands | 1.0 total | 0.05 fish<br>0.3 crustaceans<br>1.0 molluscs | | 0.5 fish & crustaceans<br>2.0 molluscs & shellfish | |
| Belgium | 0.3 All fish products | | | | |
| Spain | 0.5 | | | | |
| Italy | 0.7 | 2.0 | | 2.0 | |
| Denmark | 0.5 | | | | |
| Norway | 0.3 total<br>0.2 Methyl | | | | |
| Sweden | 1.0 | | | 1-2 | 250 |
| Finland | 1.0 | 0.3 | 5.0 | 2.0 | 150 |
| Canada | 0.5 | | 3.5 | 0.5 | |
| Australia | 0.5 | 2.0 | 1.0 | 2.5 | 250 |