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Mercury, cadmium and lead content of canned tuna fish

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Abstract

Mercury levels in canned tuna fish were determined by cold vapour atomic absorption spectrophotometry while cadmium and lead levels were determined by flame atomic absorption spectrophotometry. The metal contents in the samples, expressed in $\mu g\,g^{-1}$ wet weight, varied from 0.20 to 0.66 with an average value of 0.29 for mercury, from 0.09 to 0.32 with an average value of 0.18 for cadmium and from 0.18 to 0.40 with an average value of 0.28 for lead. The results of this study indicate that tuna fish from the Mediterranean coast of Libya have concentrations well below the permissible levels for these toxic metals. Their contribution to the body burden can therefore be considered negligible.

1. Introduction

Toxicological and environmental studies have prompted interest in the determination of toxic elements in food. While mercury, cadmium and lead can be tolerated only at extremely low levels, at certain concentrations they are exceptionally toxic to humans.

Fish accumulate substantial concentrations of mercury in their tissues and thus can represent a major dietary source of this element to humans. With the exception of occupational exposure, fish are acknowledged to be the single largest source of mercury for man. In some instances fish catches were banned for human consumption because their total mercury content exceeded the maximum limits recommended by the Food and Agriculture/World Health Organisation (FAO/WHO, 1972). Takizawa (1979) cited the case where several major incidents of human poisoning in Japan (at Minamata) were implicated in the ingestion of methylmercury-contaminated fish in large quantities. The likelihood of mercury toxicity from fish consumption has been identified in Peru and some coastal regions of the Mediterranean (Inskip & Piotrowski, 1985; Piotrowski & Inskip, 1981).

Tuna was recognised as a predator able to concentrate large amounts of heavy metals. For example, Enomoto and Uchida (1973) reported mercury concentrations ranging from 50 to $120\,\mu g\,g^{-1}$ in internal organs of Japanese tuna. The ingestion of food is an obvious means of exposure to metals, not only because many metals are natural components of foodstuffs, but also because of environmental contamination and contamination during processing. Solder used in the manufacture of cans is a recognised source of contamination of food by lead during canning. The presence of heavy metals, and particularly mercury, in the environment has been a matter of concern since their toxicity has been clearly documented (Uchida, Hirakawa & Inoue, 1961). The presence of mercury in the environment was reviewed (Holden, 1973; Krenkel, 1973). Extensive surveys have been carried out, in a number of countries, to evaluate the presence of heavy metals in the aquatic biota, including fish, which can often be considered as indicators of marine pollution. Levels of heavy metals including mercury, lead and cadmium, in fish, have been widely reported (Hellou, Warren, Payne, Belkhode & Lobel, 1992; Joseph & Srivastava, 1993; Kowalewska & Korzeniewski, 1991; Sharif, Mustafa, Mirza & Safiullah, 1991; Sharif, Mustafa, Hossain, Amin & Safiullah, 1993; Winchester, 1988). The toxic nature of certain metals and the major contribution made to the total body burden of these metals by food consumption are well documented (Bonner & Bridges, 1983; Browning, 1969; Department of Health and Social Security, DHSS, 1980). Hence the levels of these metals in foodstuffs are under frequent review.

Canned tuna fish are frequently and largely eaten in Libya, so their toxic metal content should be of some concern to human health. The present study was, therefore, carried out in view of the scarcity of information

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about heavy metals in marine organisms from this region. In this paper, the levels of mercury, cadmium and lead in samples of canned tuna fish are reported. It is hoped that the results of this study will help in generating data needed for the assessment of toxic metal intake from this source.

2. Materials and methods

2.1. Apparatus

All glassware was soaked overnight in 10% (v/v) nitric acid. Glassware, for the analyses of lead and cadmium was rinsed thoroughly with deionised distilled water and dried before use, and that for mercury analyses was rinsed with distilled water. This was to control the possible mercury contamination of water from the resins used in deionisers.

A Perkin-Elmer Model 2380 atomic absorption spectrophotometer equipped with a deuterium background corrector was used for the determination and the mercury/hydride generator was a Perkin–Elmer Model MES-10 with an open quartz tube. The signals were obtained on a Perkin-Elmer PRS-10 Printer Sequencer.

2.2. Reagents

All reagents used were of analytical reagent grade (BDH Chemicals Ltd, Poole, England). Standard stock solutions of lead, cadmium and mercury were prepared by diluting concentrated solutions to obtain solutions of 1000 mg l^{-1} (E. Merck).

The working solutions were freshly prepared by diluting an appropriate aliquot of the stock solutions through intermediate solutions using 5% HNO_3 for diluting lead and cadmium solutions, and 1 M HCl for diluting mercury solution. Stannous chloride was prepared fresh by dissolving 10 g in 100 ml of 6 M HCl. The solution was boiled for about 5 min, cooled, and nitrogen bubbled through it to expel any mercury impurities. Diluting solution for mercury determination was prepared by diluting 100 ml of conc HNO_3 and 25 ml of conc H_2SO_4 to 1000 ml with distilled water.

2.3. Sample preparation and digestion

Tuna fish caught by commercial vessels from the Mediterranean coast of Libya are canned as chunks at a commercial factory on land. Fifty cans of tuna (5 kg each) obtained from the Tuna Canning Factory in Misurata, Libya were used for this study. After opening each can, oil was drained off and the meat was homogenized thoroughly in a food blender with stainless steel cutters. Samples were then taken and digested promptly.

The homogenised sample (1 ± 0.01 g) was weighed into a 100 ml Erlenmeyer flask and 1 ml of conc HCl was added. After about 10 min, 5 ml of conc HNO_3 was added slowly. After swirling gently, 2 ml of (1 + 1) H_2SO_4 was added. It was then covered with a watch glass and left at room temperature until most of the sample had dissolved. The flask was then placed on top of a steam bath until complete dissolution. It was then removed from the steam bath, cooled and the solution transferred carefully into a 20 ml volumetric flask and diluted to the mark with distilled water. For each run, a duplicate sample, spiked samples, and two blanks were carried through the whole procedure.

For the determination of lead and cadmium, about 10 ± 0.01 g was weighed into a 150 ml beaker and 10 ml of freshly prepared 1:1(v/v), H_2O_2 (30%):HNO_3(conc) was added per gram of sample, slowly, in portions. The beaker was covered with a watch glass and, after most of the sample had dissolved, heated on a hot plate until the solution was clear. Heating was continued until the volume was reduced to about 5 ml. The solution was allowed to cool, transferred into a 20 ml volumetric flask and diluted to the mark with deionised distilled water. For each run, a duplicate sample, spiked samples and two blanks were carried through the whole procedure.

2.4. Determination of recovery

The recoveries of the metals were determined by adding increasing amounts of mercury, cadmium and lead to samples which were then taken through the digestion procedure. The resulting solutions were analysed for the metal concentrations. The results are reported in Tables 1–3. The mean recoveries for lead, cadmium and mercury were 99.8, 99.3 and 97.2, respectively, with coefficients of variation 8.7, 3.8 and 3%, respectively.

2.5. Chemical analysis

Lead and cadmium were determined by direct aspiration of the sample solutions into the air/acetylene flame. The blanks and calibration standard solutions were also analysed as the sample solutions and calibration curves constructed. Mercury was determined by the MES-10 Mercury/Hydride system with a modification in the operation. The manufacturer's operating procedure involves continuous addition of sodium borohydride solution from a reluctant reservoir with the aid of argon gas until maximum absorbance is produced. This procedure was, however, found to give poor reproducibility because the volume of sodium borohydride added each time varies. In this study, the reluctant reservoir was left empty. An aliquot of the sample solution (5 ml) was diluted to 30 ml in the reaction flask with the diluting acid solution and 2 ml of the stannous chloride solution was added. The reaction flask was immediately

connected to the system and the plunger actuated immediately, allowing argon to bubble through the solution after flowing through the empty reservoir. During this period, any mercury vapour generated is swept into the absorption quartz cell aligned in the light path of the mercury hollow cathode lamp where the absorption is measured. Aliquots of the calibration standard solutions and blanks were analysed in the same way as the samples.

3. Results and discussion

Fifty samples of canned tuna fish from Misurata canning factory were analysed for lead, cadmium and mercury. Good recoveries of spiked samples demonstrate the accuracy of the methods used (Tables 1–3).

Of the 50 samples analysed, mercury was detected in 20 samples, while lead and cadmium were detected in only 12 samples. The concentrations of lead, cadmium and mercury are presented in Table 4 as means with standard deviation and coefficient of variation. The results of the analysis indicate that the concentration of cadmium varied from 0.09 to 0.32 with a mean of $0.18\,\mu g\,g^{-1}1$; for lead it ranged from 0.18 to 0.40 with a mean of $0.28\,\mu g\,g^{-1}$. Good agreements were observed when our results were compared with those reported by other authors (Committee for Inland Fisheries of Africa CIFA, 1992). The cadmium concentrations were low compared to fish from the coast of Philippines and the Northern Indian Ocean (CIFA, 1992). Woidich and Pfanhauser (1974) reported a concentration range of cadmium in tuna fish ($0.050–0.970\,\mu g\,g^{-1}$) within which our values fell. Muller and Forstner (1973), however, reported higher levels of cadmium ($10–40\,\mu g\,g^{-1}$) in fishes from Necker and Ems. Teherani, Stehlik, Tehrani and Schada (1979) reported $0.1–0.13\,\mu g\,g^{-1}$ cadmium in several fish types caught in upper Austrian waters,

Table 1
Recovery of lead from canned tuna samples

Sample no.	Sample weight (g)	Concentration of lead ($\mu g\,g^{-1}$) added	Concentration of lead ($\mu g\,g^{-1}$) recovered	% Recovery
9	10	0.20	0.18	90
9	10	0.40	0.41	103
9	10	1.00	0.96	96
9	10	2.00	2.20	110

Table 2
Recovery of cadmium from canned tuna samples

Sample no.	Sample weight (g)	Concentration of cadmium ($\mu g\,g^{-1}$) added	Concentration of cadmium ($\mu g\,g^{-1}$) recovered	% Recovery
9	10	0.10	0.10	100
9	10	0.20	0.19	95
9	10	0.50	0.52	104
9	10	1.00	0.98	98

Table 3
Recovery of mercury from canned tuna samples

Sample no.	Sample weight (g)	Concentration of mercury ($\mu g\,g^{-1}$) added	Concentration of mercury ($\mu g\,g^{-1}$) recovered	% Recovery
10	1	0.02	0.0202	101
10	1	0.05	0.0490	98
10	1	0.10	0.0980	98
10	1	0.20	0.1920	96

Table 4
Mean contents of mercury, cadmium and lead ($g\,g^{-1}$) in canned tuna samples

Metal	No. of samples	Range	Mean	Standard deviation	Coefficient of variation (%)
Mercury	20	0.20–0.66	0.29	0.12	40.7
Lead	12	0.18–0.40	0.28	0.07	24.3
Cadmium	12	0.09–0.32	0.18	0.08	42.2

which are lower than values reported here. The concentration of lead was found to be less than $0.35\,\mu g\,g^{-1}$ in most of the samples, which agrees well with values reported by other authors (CIFA, 1992; Woidich and Pfanhauser, 1974).

The concentration of mercury in the tuna fish samples analysed varied from 0.2 to $0.66\,\mu g\,g^{-1}$. Apart from two samples which have concentrations of 0.55 and $0.66\,\mu g\,g^{-1}$ mercury, all the samples have concentrations below the $0.5\,\mu g\,g^{-1}$ limit recommended by the FAO/WHO (1972) and adopted by many countries (CIFA, 1992). The levels of the toxic metals in the tuna samples are not high when compared to some other areas of the world. The mercury content of tuna fish has variously been reported as ranging from 0.8 to $1.20\,\mu g\,g^{-1}$ with an average content that is between 0.3 and $0.4\,\mu g\,g^{-1}$ (Holden, 1973), below which our values fall. Mean mercury levels reported here are lower by an order of magnitude compared to values reported for mullets in the Tyrrhenian Sea, an area close to naturally occurring mercury deposits (CIFA, 1992). However, they were similar to levels in other tropical, less industrialised areas like Indonesia, Thailand and Papua New Guinea (CIFA, 1992). A similar trend was observed when our values were compared with values ($0.04–0.44\,\mu g\,g^{-1}$) reported for canned salmon and tuna and values ($0.009–0.73\,\mu g\,g^{-1}$) reported for canned sea food (Fricke, Robbins & Caruso, 1979; Kaiser & Tolg, 1980).

With respect to the heavy metal content of marine organisms taken from other Mediterranean coastal areas, very little comparison data appear to be available. However, our results compare well with values reported for fish from the Mediterranean coast of Israel (Hornung & Kress, 1989; Roth & Hornung, 1977) and that of Morocco (El-Hraiki, Kessabi, Sabhi, Benard & Buhler, 1992).

Because of the bioaccumulation of mercury by fish and shellfish, these food items can be a rich source of metal (Buzina, Suboticanec, Vukusi'c, Sapunar, Anton'ic & Zorica, 1989; Piotrowski & Inskip, 1981). As a consequence of its known toxicity, as well as that of lead and cadmium and of the serious contamination of foods that occurs from time to time during commercial handling and processing, most countries monitor the levels of toxic elements in foods. The Joint Food and Agriculture Organisation/World Health Organisation (FAO/WHO) Expert Committee on Food Additives has suggested a provisional tolerable intake of 400–500 μg cadmium per week for man; the quantity of mercury to be tolerated in human food is 0.3 mg per week and, for lead, a weekly intake of 3 mg (FAO/WHO, 1972). The maximum concentration of lead which is permitted in prepared foods specifically intended for babies or young children is $200\,\mu g\,kg^{-1}$ (FAO/WHO).

Although, marine food does not significantly contribute to the chronic lead body burden, the monitoring of lead concentration in the diet is essential since fish of various types were found to be contaminated with lead in addition to cadmium and mercury. Lead concentrations could be high in marine animals that live on sediment.

Though estimates of the amount of toxic metals consumed in the diet are difficult to obtain and a discussion of metal tolerances in the diet is beyond the scope of this paper, it can be concluded from the results so far obtained that mercury, lead and cadmium content of the canned tuna fish is unlikely to constitute a significant health hazard.

References

Bonner, F. W., & Bridges, J. W. (1983). Toxicological properties of trace elements. In J. Rose, *Trace elements in health* (pp. 1–20). London: Butterworth.

Browning, E. M. (1969). *Toxicity of Industrial Metals* (2nd ed.) London: Butterworth.

Buzina, R., Suboticanec, K., Vukusi'c, T., Sapunar, J., Anton'ic, K., & Zorica, M. (1989). Effect of industrial pollution on seafood content and dietary intake of total and methylmercury. *Science of the Total Environment, 78*, 45–57.

CIFA (Committee for Inland Fisheries of Africa) (1992). Report of the Third Session of the Working Party on Pollution and Fisheries, FAO Fisheries Report No 471, Food and Agriculture Organisation of the United Nations, Rome.

DHSS (Department of Health and Social Security) (1980). Lead and health: the report of a DHSS working party on lead in the environment. London: HMSO.

El-Hraiki, A., Kessabi, M., Sabhi, Y., Benard, P., & Buhler, D. R. (1992). Contamination of seafood products by cadmium, chromium, mercury and lead in Morocco. *Rev. Med. Vet., 143*, 49–56.

Enomoto, N., & Uchida, Y. (1973). Cadmium and other heavy metal contents in marine products from the Ariake Sea and in canned goods on the market. *Saga Daigaku Nogaku Iho*, *35*, 1973, 69–75 [Cited in *Chem. Abstr. 18* (1974) 2506].

Food and Agriculture/World Health Organisation (FAO/WHO) (1972). Evaluation of certain food additives and the contaminants mercury, cadmium and lead. WHO Technical Report Series No. 505. Geneva: WHO.

Fricke, F. L., Robbins, W. B., & Caruso, J. A. (1979). Trace element analysis of food and beverages by atomic absorption spectrometry. *Progress in Analytical Atomic Spectroscopy, 2*, 185–286.

Hellou, J., Warren, W. G., Payne, J. F., Belkhode, S., & Lobel, P. (1992). Heavy metals and other elements in three tissues of cod, *Gadus morhua* from the Northwest Atlantic. *Marine Pollution Bulletin, 24*, 452–458.

Holden, A. V. (1973). Mercury in fish and shellfish, a review. *Journal of Food Technology, 8*, 1–25.

Hornung, H., & Kress, N. (1989). *Trace elements in offshore and inshore fish from the Mediterranean coast of Israel*. 5th International Congress on Environmental Pollution and its impact on life in the Mediterranean Region, Blanes (Spain), 2–6 October 1989.

Inskip, M. J., & Piotrowski, J. K. (1985). Review of the health effects of methylmercury. *Journal of Applied Toxicology, 5*, 113–133.

Joseph, K. O., & Srivastava, J. P. (1993). Mercury in the Ennore estuary and in fish from Madras coastal waters. *Journal of Environmental Biology, 14*, 55–62.

Kaiser, G., & Tolg, G. (1980). Mercury. In O. Hutzinger, *The handbook of environmental chemistry* (pp. 1–58). New York: Springer Verlag.

Kowalewska, M., & Korzeniewski, K. (1991). Trace metals in *Gasterosteus aculeatus* L. from the Gdansk Bay. *Pol. Arch. Hydrobiology, 38*, 475–484.

Krenkel, P. A. (1973). Mercury, environmental considerations, Part 1. CRC Crit. Rev. In *Environmental Control* Saf. Manage. May, 303–73.

Muller, G., & Forstner, U. (1973). *Naturwissenschaften 60*, 258–265.

Piotrowski, J. K., & Inskip, M. J. (1981). Health effects of methylmercury. AMRC Technical Report 24, MARC.

Roth, I., & Hornung, H. (1977). Heavy metal concentrations in water, sediments and fish from Mediterranean coastal area, Israel. *Environmental Science and Technology, 11*, 265–269.

Sharif, A. K. M., Mustafa, A. L., Hossain, M. A., Amin, M. N., & Safiullah, S. (1993). Lead and cadmium contents in ten species of tropical marine fish from the Bay of Bengal. *Science of the Total Environment, 113*, 193–199.

Sharif, A. K. M., Mustafa, A. L., Mirza, A. H., & Safiullah, S. (1991). Trace metals in tropical marine fish from the Bay of Bengal. *Science of the Total Environment, 107*, 135–142.

Takizawa, Y. (1979). Epidemiology of mercury poisoning. In J. O. Nriagu, *The biogeochemistry of mercury in the environment* (pp. 325–365). Amsterdam: Elsevier.

Teherani, D. K., Stehlik, G., Tehrani, N., & Schada, H. (1979). *Environmental Pollution*, *18*, 241–249.

Uchida, M., Hirakawa, Y., & Inoue, T. (1961). Biochemical studies on Minamata disease IV. Isolation and chemical identification of the mercury compound in the toxic shellfish with special reference to the causal agent of the disease. *Kumamoto Medical Journal, 14*, 181–184.

Winchester, R. V. (1988). Trace metal levels in fish from the Manukau Harbour, Auckland, New Zealand, related to a water pollution incident. *New Zealand Journal of Marine Freshwater Research, 22*, 621–624.

Woidich, H., & Pfanhauser, W. (1974). *Z. Lebensm Unters Forsch 155*, 72–76.