Metal toxicity and environmental effects on health: a study report on mineral and heavy metal contents of different Malaysian fish species

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Abstract
This paper discusses effects of metal toxicity and environment on health and followed by a study report on mineral and heavy metal contents of fish conducted in Malaysia as an example. Fish, a part of being a good source of digestible protein vitamins, minerals and polyunsaturated fatty acids (PUFAs), are also an important source of heavy metals. Some of the metals found in the fish might be essential as they play important role in biological system of the fish as well as in human being, some of them may also be toxic as might cause a serious damage in human health even in trace amount at a certain limit. A comprehensive study was conducted to fishes collected in Langkawi Island, a popular tourist destination in Malaysia and the overall findings revealed that from the human health point of view, the fin is a type of fish found in the coastal areas of the island are safe for the consumption. The mineral and heavy metal contents are within the allowable limit of consumption.

Introduction
Fish are popularly recognized as an excellent source of lipids that are composed of a wide range of important fatty acids. Fish also contain good quality protein and are an adequate source of many vitamins (e.g. fat-soluble A, D, E and the water-soluble B-complex), in addition to important minerals such as calcium and phosphorous. Lipids derived from fatty fish, in particular, contain high proportions of highly polyunsaturated fatty acids that confer considerable developmental and health benefits to consumers. For example, specific fish species that contain high content of lipids rich in the long chain n-3 polyunsaturated fatty acids (LC-PUFA), especially eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA), have an important role in human nutrition for optimal human growth and development, prevention of chronic disease and overall health promotion (Cunnane et al., 2000; Birch et al., 2000; Stark and Holub, 2004; Salem et al., 2001). These particular LC-PUFAs are considered “semi-essential” nutrients to human and most animal species because of the fact that mammals are not efficient at synthesizing them to appreciable levels, thus making dietary sources such as fish consumption one of the more realistic ways in which intake is ensured.

In addition to high-quality lipids having important roles in nutrition, it is also true that all living organisms require adequate intakes of bioavailable minerals, including calcium, copper, iron, manganese, and zinc, as well as trace amounts of some trace metals, including molybdenum, vanadium and strontium. Although these minerals and metals are essential to some degree for specific roles that maintain homeostasis in many biological systems common to both fish and humans’ welfare, they can also be toxic to both human and fish at specific high concentrations.

The ocean is also an important source of non-essential heavy metals, such as cadmium, chromium, mercury, lead, arsenic and antimony (Kennish, 1992). Industrial and agricultural activities are the leading potential source of pollutant accumulation in the aquatic environment including ocean seas (Tarras-Wahlberg et al., 2001; Akif et al., 2002). Waste materials that gain access to the seas can accumulate in sediments and in marine organisms, including fish, which co-exist in this environment, thus being the source of transfer to humans through a food chain (Tüzen, 2003). Given that humans in many cultures consume large quantities of fish, thus exposed to the increased probability of consuming large amounts of accumulated metals, the concentration of heavy

Keywords
Mineral
Heavy metals
Toxicity
Malaysia
Fin fish

Article history
Received: 24 November 2017
Received in revised form: 14 December 2017
Accepted: 14 December 2017
metals in commercial fish is an important human health factor that requires proper assessment in order to estimate the risks to human health posed by fish consumption (Cid et al., 2001).

This paper discusses effects of metal toxicity and environment on health and followed by a study report on mineral and heavy metal contents of fish conducted in Malaysia as an example.

**Heavy metal toxicity and environmental health impact**

Heavy metals are defined as metallic chemical elements that have a relatively high density and are toxic or poisonous at low concentrations. According to Kennish (1992), heavy metals are elements having atomic weights between 63.546 and 200.590 and the specific gravity of most of them is > 4.0. Examples of heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), lead (Pb), chromium (Cr), cobalt (Co), and thallium (Tl) (Somer, 1974). Risk assessment of heavy metal exposure results in categorizing them as being hazardous to human health, because of the potential for bioaccumulation, a process where levels increase in biological organisms over time above and beyond that compared with the environmental concentration. Heavy metals of particular concern to surface water systems are Cd, Cr, Hg, Pb, As, and antimony (Sb) (Kennish et al., 1992), which poses a serious threat because of toxicity, persistence and biomagnification in the food chain (Begum et al., 2005). The presence of metals entering the aquatic environment and the food chain are due particularly to natural processes, such as volcanic activity and weathering, dissolution, vaporization and biological processes that involve man-made pollution (e.g. agriculture and industrial waste (Mansour and Sidky, 2002)). Industrial (e.g. caustic soda production, pulp and paper preservative, electrical devices) and agricultural (fungicides, seed preservatives) activities comprise the leading sources of accumulating heavy metal pollutants in aquatic environments including the sea (Freedman, 1989; Güngüm et al., 1994; Nimmo et al., 1998; Barlas, 1999; Tarras-Wahlberg et al., 2001; Akif et al., 2002; Jordao et al., 2002).

Toxicity of heavy metals is dependent on the specific chemical form present in the food chain. For example, mercury poisoning is less toxic when present in organic form than either metallic or ionic form (Hattula et al., 1978). Chemical waste streams that enter the sea and accumulate in sediments and marine organisms, including fish, can consequently be transferred to humans through the food chain (Tüzen, 2003).

Heavy metal contamination of foodstuffs can cause serious health hazards such as the nephritis, anuria and extensive kidney lesions that are caused by Cr, zinc (Zn) and copper (Cu) poisoning (Mansour and Sidky, 2002). Pb contamination causes renal failure and liver damage, whereas Cd and Hg damage the kidneys and cause symptoms of chronic toxicity, including impaired kidney function, poor reproductive capacity, hypertension, tumors and hepatic dysfunction (Mansour and Sidky, 2002).

Bioaccumulation of heavy metals by aquatic organisms will lead to greater exposure of these materials in the food chain. Heavy metals that accumulate in marine organisms often reflect, in part, the ubiquitous nature of the metals, and can vary in regard to the chemical form as well as the extent of biotransformation that results due to subsequent metabolism by marine plant or animal organisms. Cd is widely distributed in the aqueous environment, and bioaccumulation of the metal has been well researched. In the case of Hg and Pb contamination of seafood sources, several comprehensive worldwide surveys have been conducted to assess human Hg exposure from fish contaminated with these metals. Various forms of Hg that enter the aquatic environment as a result of both natural geologic or human pollution activities may be converted to methylmercury, which in-turn can be concentrated in edible fish muscle. Organic mercury poisoning has been linked to methylmercury pollution of aquatic food sources in different countries such as Canada, Sweden and Japan. Methylmercury is relatively speaking, yields greater chronic toxicity than other forms of Hg. Pb which is released mostly from the atmosphere and other sources into the aquatic environment is a public health concern because is regarded as a potential sink for Pb-containing pollutants. The physicochemical form of Pb will influence the degree of uptake by the marine life. For example, at normal pH of ocean water, Pb is more than likely to be precipitated as PbCl₂; acidification will increase the bioavailability of the element by affecting speciation or the shift in equilibrium to a free divalent anion.

Several countries have extensively surveyed heavy metal residue levels in the aquatic biota, including fish, which in some instances are considered indicators of marine pollution. Heavy metal discharge into the marine environment has been a cause of considerable worldwide concern due to toxicity and related accumulative behaviour. Some fish species accumulate Hg, Pb, and Cd to potentially high and toxic levels through bioaccumulation (Hattula et al., 1978; Sharif et al., 1991). For example, marine life can accumulate Cd directly from the water through gills or skin and deposit it into tissues that will have...
concentrations much greater than that found in their ambient environment.

Fish catches in certain countries that are exposed to environmental heavy metal pollution have been banned for human consumption because of excessively high total heavy metal content which exceeds the maximal limits recommended by the Food and Agriculture/World Health Organization (FAO/WHO, 1972). Takizawa (1979), cited Minamata disease that was caused by ingesting fish contaminated with large quantities of methylmercury in Southern Japan. The likelihood of mercury toxicity from fish consumption has also been identified in Peru and some coastal regions of the Mediterranean (Inskip and Piotrowiski, 1981, 1985).

Heavy metal accumulation in various fish species has been studied in different marine ecosystems (Kucuksezgin et al., 2001 Lewis et al., 2002; Mansour and Sidky, 2002 Turkmen et al., 2004; Begum et al., 2004) in order to determine the risk to human health (Cid et al., 2001). A common finding from these studies has been that metal accumulation varies among and within many fish species, and furthermore, is associated with gender, biological cycle and organ part of the fish analyzed. Moreover, ecological factors such as season, place of development, nutrient availability, temperature and salinity of the water are additional variables that can contribute to wide ranges of metal concentrations in fish flesh.

Metal and mineral contents in Malaysian waters and fish species

Recent efforts have been made to quantitate the concentrations of heavy metals, such as Hg, Pb and Cd in fish caught off the coast of Langkawi Island in Malaysia, as well as in its waters. The same fish were also used to determine the content of nutritional minerals, such as Cu, Zn, calcium (Ca), and manganese (Mn).

Fish and water samples were collected from four different areas, namely (1) Main Jetty Pulau Tuba (MJPT), (2) Teluk Cempedak Jetty (TCJ), (3) Simpang Tiga Chian Lian (STCL) and (4) Main Jetty Kuah (MJK) around Langkawi Island. Surface (0-15 cm depth) and bottom (20-34 cm depth) waters were collected into 21 ml samples and representative aliquots were transferred into polypropylene bottles. Fish samples were washed with clean sea water at the point of collection, separated by species and location and packed in polyethylene plastic bags inside a cooler. After reaching the laboratory, the samples were stored at -27°C. We used atomic absorption spectrophotometry (AAS) to analyze the heavy metal contents in 8 fish species, as seen in Table 1. The instrument was calibrated using commercially available standards and the inert gas for sample analysis was high purity argon.

Metal contents in Malaysian Waters

Table 2 shows the metal concentrations in water samples collected from four key locations in Langkawi coastal areas were comparable. Mean values of Zn and Cd were generally low (Zn and Cd ≤ 0.02 ppm) at all four locations and did not significantly differ between the surface and bottom samples. However, Hg values although very low, differed between the surface and bottom samples collected from all locations. Surface samples from MPJT and TCJ contained more Hg (0.004 and 0.003 ppm, respectively) than bottom samples (0.001 ppm in both locations), whereas water from the bottom of MJK contained more Hg (0.007 ppm) than that from the surface (0.002 ppm). The Hg contents of surface and the bottom samples from STCL did not significantly differ.

Cu contents ranged from 2.77 to 4.00 ppm at the four sites, and from 2.77 and 2.85 ppm in bottom and surface samples collected from MJK. The respective values at STCL were significantly higher at 3.90 and 4.00 ppm, respectively. The bottom and surface values in samples collected at MJPT and TCJ were 3.05 and 3.02, and 3.81 and 3.65, respectively. Table 2 shows that the Cu contents significantly differed between the surface and the bottom at all locations.
The Pb contents of water samples varied among locations. The lowest surface and bottom values of 1.58 and 2.08 ppm, respectively were found at MPJT. The other surface and bottom values were as follows: TCJ, 2.87 and 3.04, STCL, 3.61 and 4.50 and MJK, 4.73 and 3.74 ppm, respectively.

The Mn contents of all samples ranged from 0.41 to 0.44 ppm and did not significantly differ among the four locations, or between the surface and the bottom of each location. Calcium values ranged from 25.85 to 27.89 ppm. The values were higher at the surface than at the bottom of MJPT (27.89 vs. 25.93 ppm) but did not significantly differ between the surface and the bottom of the other 3 locations.

Mineral contents of different Malaysian fish species.

Minerals that fall into the category of being vital to include Cu, Zn, Ca, and Mn. Common to many marine organisms that are a ready source of dietary nutrients for humans is the bioavailable vital minerals such as potassium (K), chlorine (Cl), phosphorous (P), iron (Fe), iodine (I), Cu, Ca, Zn and Mn.

The Zn concentration was highest among all the vital minerals tested and generally ranged from 34.33 (“kembong”, Psettodes crumei) to 49.39 ppm (“jenahak”, Epinephelus sexfasciatus). Table 3 shows that the Cu and Mn contents of the fish ranged from 11.48 to 13.95 ppm and from 6.18 to 24.35 ppm, respectively. “Kembong” (Psettodes crumei) contained the most Cu, followed by “kintan” (Arius cumatranus) (12.75 ppm) and “malong” (Rastrelliger kanagurta) (12.68 ppm), whereas “kerapu” (Cynoglossus lingua) contained the least. “Malong” (Rastrelliger kanagurta) contained the most Mn and both “kembong” (Psettodes crumei) and “Kintan” (Arius cumatranus) contained the least. Ca levels ranged from 5.66 to 15.1 ppm. “Jenahak” (Epinephelus sexfasciatus) contained the least, whereas “kembong” (Psettodes crumei) and “kintan” (Arius cumatranus) contained the most. Unlike other elements, limits have not been set for Cu and Mn in either the FAO or the Malaysian guidelines. Table 3 also indicates that the Zn content of all of the fish species studied herein was far below the FAO recommended a limit of 150 ppm and the Malaysian standard of 100 ppm. The concentration of Cu was slightly higher, whereas that of Mn was almost triple the FAO limits. However, the Cu concentration was lower than the Malaysian Food and Regulation limit (1985).

Heavy metal contents in different Malaysian fish species.

Table 3 also shows the heavy metal contents of 8 fish species found off Langkawi Island. Heavy metal contamination in fish is normally compared to the permissible limits recommended by Food and Agriculture Organization and World Health Organisation (FAO/WHO, 1984). However, the Ministry of Health Malaysia has also established its own standards called the Malaysian Food Regulation (1985). Table 4 reports the mean concentrations of...
heavy metals found in various fish species compared with the permissible limits established by the FAO and the Malaysian Government. The mean values of toxic Pb and Hg were below the FAO permissible limits (1984), whereas that of Cd was slightly higher than the FAO limit but within the Malaysian Food Regulations (1985).

The metal levels in the fish evaluated herein were comparable to those found by earlier Malaysian studies (Table 4). However, the results showed that the heavy metal concentration is increasing since the present values are almost double those in the earlier reports. The metal concentrations in water (Table 2) and fish (Table 3) varied. Water contained more Ca and Pb, but less Mn, Zn and Cd than fish. The Hg concentration in fish was almost equal to that in water. This difference may be due to the fact that heavy metals are not digested or excreted efficiently by the fish and tend to accumulate (Tüzen, 2003).

Significance of exposure to mineral and metal content from Malaysian fish

The Malaysian population consumes approximately 160 g/day of fish (FAO, 2005). This figure is the highest among the countries in South-East Asia (ASEAN countries). The rate of fish consumption for an Indonesian, for example, is only 57 g/day, whereas the rates for a Cambodian and a Thailand are 71 and 85 g/day, respectively.

Since seafood is one of the most important food sources in Malaysia, intake of metals or trace elements from seafood, especially toxic elements, is of great concern for human health risk. To evaluate the health risk to people in the country through consumption of marine fish, daily intake of metals was estimated on the basis of concentrations (wet wt. basis) of the metals in the muscle of fish and daily fish consumption.

U.S. Environmental Protection Agency (U.S. EPA, 2005) has published reference doses (RfD) for several trace elements. According to this agency, Rfd of Cu is (40 µg/kg body wt./day), while Rfds for other elements are as follows: Mn (140 µg/kg body wt./day), Zn (300 µg/kg body wt./day), Cd (1 µg/kg body wt./day) and MeHg (0.1 µg/kg body wt./day). We assumed that concentration of total Hg is equal to that of MeHg in muscle in the present study. No values have been set for Ca and Pb by U.S. EPA.

The 61st meeting of the Joint FAO/WHO Expert Committee on Food Additives (JECFA) (JECFA, 2003) has also established a provisional tolerable weekly intake (PTWI) of 1.6ug/kg body wt./week (0.23 µg/kg body wt./day for Hg. Since RfDs of Pb was not established by EPA, PTWI of 25ug/kg body wt./week (=3.57 µg/kg body was used for risk assessment in the present study. Average body weight of Malaysian adult people was assumed to be 50 kg, and the guideline for heavy metals and minerals were calculated from RfDs and PTWI and the body weight. A guideline for Cu (2000), for

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<th>Table 3. Heavy metal content of selected fin fish from Langkawi Island coastal area in Malaysia</th>
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†Values are means of triplicate analyses of each species; †Malaysian Food regulation (1985); ND, undetectable.
example, was calculated by multiplying the RFD for Cu (40 µg/kg body wt./day) with 50 kg body weight. A Malaysian adult consuming “jenahak” (Lutjanus agentimaculatus), for example, will have 1840 µg intake of Cu daily (11.55 ppm X 160 g/day).

Table 5 shows estimated daily intakes and guideline value for trace metals for different fish species studied. For vital mineral, dietary intakes varied from 1848 to 2232, while the guideline value is 2000. Mn and Zn were consumed by Malaysian people much below their tolerable daily intakes.

For toxic Pb metal, estimated daily intake of people in Malaysia through different fish species examined herein was lower than the guideline limit. The daily intake for Pb ranged from 128 to 176, while the guideline value was 179. Except for Cd in “duri” (Arius cumatranus) and Hg in “jenahak” (Lutjanus agentimaculatus), the dietary intake of heavy metals through fish species evaluated in this study were lower than the guideline values. Intake of Cd in “duri” (Arius cumatranus) was 144 and the intake of Hg in “jenahak” (Lutjanus agentimaculatus) was 176. The guideline values for the two toxic metals were 50 and 11, respectively.

**Conclusion**

Seafood-origin proteins and fatty acids play an important role in the human diet. The PUFAs are crucial in terms of human feeding physiology.
Moreover, though fish is known as a good source of digestible protein, vitamins, minerals and polyunsaturated fatty acids (PUFA), are also sources of heavy metals which, beyond a certain limit, are toxic for human consumption. The overall findings reveal that from the human health point of view, fish found in Langkawi Island coastal areas are safe for the consumption. The mineral and heavy metal contents are within the allowable limit of consumption.

References


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