Environ Monit Assess (2013) 185:6407–6412
DOI 10.1007/s10661-012-3033-y

Analysis of mercury, selenium, and tin concentrations in canned fish marketed in Iran

S. V. Hosseini · F. Aflaki · S. Sobhanardakani · L. Tayebi · A. Babakhani Lashkan · J. M. Regenstein

Received: 7 June 2012 / Accepted: 27 November 2012 / Published online: 12 December 2012

Abstract The presence of heavy metals in the environment could constitute a hazard to food security and public health. These can be accumulated in aquatic animals such as fish. In the present paper, three heavy metals (mercury, selenium, and tin) in canned products produced and sold in Iran were studied: longtail tuna, Kawakawa, Kilka, and yellowfin tuna were determined using inductively coupled plasma–optical emission spectrometer and a direct mercury analyzer. Analytical results were validated by spiking the samples with various concentrations of these metals to test recovery. The metal contents, expressed in micrograms per gram, wet weight, varied depending upon the species studied. The levels of Hg ranged from 0.0003 to 0.408 μg/g, the levels of Sn ranged from 0.036 to 0.480 μg/g, while the levels of Se ranged from 0.130 to 4.500 μg/g. Comparative evaluation of these metals in different brands of canned fish showed that the average concentrations of Hg, Sn, and Se of all species is significantly lower than adverse level for the species themselves and for human consumption when compared with FAO/WHO permissible limits. Therefore, their contribution to the total body burden of these heavy metals can be considered as negligibly small.

Keywords Canned fish · Heavy metals · Mercury · Selenium · Tin

S. V. Hosseini (✉)
Department of Fisheries, University of Tehran,
Karaj, Iran
e-mail: hosseinisv@ut.ac.ir

F. Aflaki
Nuclear Science Research School,
Nuclear Science and Technology Research Institute,
Tehran, Iran

S. Sobhanardakani
Department of the Environment, Hamedan Branch,
Islamic Azad University,
Hamedan, Iran

L. Tayebi
Department of Fisheries, Malayer University,
Malayer, Iran

A. B. Lashkan
Department of Fisheries, University of Guilan,
Sowmeh Sara, Iran

J. M. Regenstein
Department of Food Science, Cornell University,
Ithaca, NY 14853-7201, USA

Introduction

Many chemical elements that are present in the human diet are essential for human life at low concentrations but can be toxic at high concentrations. Other elements such as Hg, Cd, Pb, and Sn have no known essential function in living organisms and are toxic even at low concentrations when ingested over a long period. Therefore, many consumers regard any presence of these elements in foodstuffs such as fish and fishery products as a hazard to health (Oehlenschläger 2005; Şireli et al. 2006). Heavy metals are considered to be the most important form of aquatic pollution because of their accumulation by aquatic organisms. Metal pollution in the marine environment is not very visible but its impacts on delicate marine ecosystems and humans can be large. Fish accumulates substantial amounts of heavy metals in their tissues especially the muscles and, thus represent a major dietary source of these metals for humans (Tariq et al. 1993; Kalay et al. 1999; Rose et al. 1999; Ashraf et al. 2006).

On the other hand, fishes and fishery products are widely consumed because of their high protein content, low saturated fat, and the presence of omega fatty acids, all of which are known to support good health (Burger and Gochfeld 2004). Several studies have documented the long-term cardioprotective benefits for adults as well as the reproductive benefits of eating fish (Burger and Gochfeld 2004). However, benefits may be offset by the presence of contaminants, particularly methylmercury (MeHg) and polychlorinated biphenyls, which have been reported in many fish species from many localities (USEPA 1998).

Hg occurs widely in the biosphere and has long been known as a toxic element presenting occupational hazards associated with both ingestion and inhalation. Hg content in fish can vary widely depending on factors such as fish species, size, position in the trophic chain, and habitat location (Ordiano-Flores et al. 2011; Sobhanardakani et al. 2011; Tayebi et al. 2011). Approximately 90 % of the human health risk related to fish consumption is associated with mercury-contaminated fish (Burger and Gochfeld 2005; Berry and Ralston 2008; Ruelas-Inzunza et al. 2008). The toxic properties of Hg have evoked increasing interest in recent years due to the extent of its use in industry and agriculture, and the recognition that the alkyl derivatives of Hg are more toxic than most other chemical forms and these compounds can enter the food chain through the activity of microorganisms with the ability to methyllate, the Hg present in industrial wastes (Underwood 1977). Exposure to heavy metals such as Hg is of immediate environmental concern. A direct relationship between heavy metal poisoning and thyroid dysfunction was reported in rabbits by Ghosh and Bhattacharya (1992).

Because Hg and, especially, methyl mercury are toxic, public concerns about the safety of seafood have been raised. However, the evidence of harm by the mercury in fish to human is scant and leading nutrition experts have in fact concluded that the health benefits of seafood, if only as nutritional sources of omega-3 fatty acids, greatly outweigh any potential risk associated with the presence of Hg (Flores-Arce 2007).

Hg and Se are naturally occurring. They are present in the environment regardless of human activity and cannot be destroyed, only transformed. Hg and Se have multiple oxidation states and complex geochemical cycles involving both inorganic and organic forms that can be found in the water, the biota, and the sediment of most bodies of water. These compound both bioaccumulate in fish tissue. But there are also significant differences between them (ASTDR 1999, 2003, 2005) although both bioaccumulate, although not equally. In discussing Hg toxicity, the fact the organisms have developed physiological mechanisms of Hg detoxification is also often ignored. An efficient mechanism of Hg detoxification involves its reaction with Se. Se is an essential trace element needed for many important physiological processes. Like Hg, it is transported along the hydrological cycle and reaches the oceans where it combines with mercury under reduction conditions to form the highly insoluble Hg (II) selenide, which ends up in marine sediments. Because Se is more abundant than Hg, not all of the oceanic Se is trapped by Hg. Enough Se remains to be taken up by plankton and other organisms in the food chain of marine animals (Flores-Arce 2007).

Hg is far and away the champion, bioaccumulating element from water to algae, then further concentrating (biomagnifying), so that in fish tissue, it is tens-of-thousands to hundreds-of-thousands times greater than its concentration in water. Selenium behaves similarly to arsenic although it seems to concentrate least strongly of the two, although this picture may depend on the chemical form(s) measured (Essig and Kosterman 2008). Se is a micronutrient element, but in high concentration causes adverse effects (Rezayi et al. 2011).

Canned fish are largely eaten in many countries, including Libya, USA, Portugal, the Kingdom of Saudi Arabia, Turkey, and Iran (Voegborlo et al. 1999; Lourenço et al. 2004; Ikem and Egeibor 2005; Khansari et al. 2005; Ashraf et al. 2006). Because of the concern for the neurotoxic effect of heavy metals such as Hg (Raymond and Ralston 2004; Bhattacharyya et al. 2010), word was done to determine the levels of Hg, Sn, and Se in 120 canned fish samples of four different brands commonly consumed in Iran.

Materials and methods

Sample collection

During the year 2012, 120 samples of four different Iranian brands (30 samples for each brand: "Famila Co." (Tehran), yellowfin tuna (*Thunnus albacares*); "Shilaneh Co." (Qazvin), common Kilka (*Clupeonella cultriventris* caspia); "Pars Tuna Co." (Bushehr), Kawakawa (*Euthynnus affinis*); and "Hiltune Co." (Tehran), longtail tuna (*Thunnus tonggol*)) of canned fish (185 g each) were analyzed for their content of Hg, Se, and Sn. These 120 canned fish samples were purchased from ten different markets in Tehran between February and April 2012.

Chemical analyses

After opening, each can content was homogenized thoroughly in a food blender with stainless steel cutters (Boadi et al. 2011). Then, samples were digested with 10 ml of 1 N HNO_3 in closed Teflon vessels in a microwave oven (CEM MARS-5 closed vessel microwave digestion system) using the following microwave digestion program: pressure of 200 psi, ramp time of 25 min, temperature of 210 °C, maximum power of 300 W, and hold of time 10 min. Then, H_2O_2 (1.5 ml, 30 %) was added to each digest to break down organic matter that may not be during the HNO_3 digestion and the same heating program was applied. After cooling, residues were transferred to 25 ml volumetric flasks and diluted to level with deionized water. Before analysis, the samples were filtered through a 0.45-μm membrane filter. Sample blanks were prepared in the laboratory in a similar manner to the field samples. All metal concentrations were determined on a wet weight basis as micrograms per gram (Turkmen et al. 2009). All samples were analyzed three times. Hg was determined by cold vapor atomic absorption using direct mercury analyzer (DMA-80) (Boadi et al. 2011). Tin and selenium were determined using inductively coupled plasma–optical emission spectrometer (Optima 2100 DV, Perkin Elmer). Standard solutions were prepared from stock solutions (Merck, multi-element standard) (Turkmen et al. 2009).

Statistical analysis

To test the differences between average concentration of heavy metals in evaluated canned fish, one-way ANOVA was performed (Tukey post-hoc). The mean levels of heavy metals were compared with international standard using a one-sample test. Probabilities less than 0.05 were considered statistically significant ($p<0.05$). All statistical analyses were performed using the SPSS 15.0 (SPSS Inc., Chicago, IL, USA) statistical package.

Results and discussion

In the present study, levels of Hg, Sn, and Se in canned fish for both domestic and export produced in Iran were determined. Table 1 shows the mean concentrations of Hg, Sn, and Se in the canned fish. The results indicate that Hg concentration in canned fish ranged from 0.0003 to 0.41 μg/g, whereas Se concentration ranged from 0.130 to 4.500 μg/g. Levels of Sn in canned fish ranged from 0.036 to 0.480 μg/g and all samples were below the detection limit for Sn. The results indicated that the average concentrations of Hg, Sn, and Se (except brands B and D) in this study are significantly lower than the adverse level for the species themselves and for human consumption with FAO/WHO and ASTDR permissible limits (0.5 μg/g

Table 1 Mean metal levels in different brands of canned fish examined in this study (in micrograms per gram wet wt)

Sample (fish and brand)	No.	Average concentration±SD		
		Hg	Sn	Se
A (longtail tuna)	30	0.092±0.01 b	0.143±0.06 a	1.592±0.24 a
B (Kawakawa)	30	0.184±0.05 d	0.171±0.05 b	2.044±0.51 c
C (common Kilka)	30	0.086±0.02 a	0.192±0.08 c	1.887±0.38 b
D (yellowfin tuna)	30	0.143±0.05 c	0.200±0.15 d	2.613±0.60 d

The letters (a, b, c, d) represent the statistical differences among different samples ($p<0.05$)

for Hg, 250.0 μg/g for Sn, and 2.0 μg/g for Se) (FAO/WHO 1984, 2009; WHO 1996, ASTDR 2003). Therefore, their contribution to the total body burden of these metals can be considered as negligibly small. Statistical grouping of the concentrations of each element in the different brands of canned fish by ANOVA and Tukey test indicated that there were significant differences within and between all of the evaluated brands ($p<0.05$) (Table 1).

Hg is known to be a very toxic metal, and fish is the most important source in the human diet (Mol 2011). The maximum limit for Hg is set by the FDA (2001) as 1.0 μg/g for fish. Similarly, the Turkish Food Codex (TFC 2002) and the European Commission Regulation 466/2001 (EU 2005) recommended 1.0 μg/g as the limit value for bonitos, but they set a limit of 0.5 μg/g for other species. Hg is especially important for species like tuna, which is well known to accumulate large amounts of this metal (Ikem and Egeibor 2005). However, Hg concentrations in tuna fish (Plessi et al. 2001; Burger and Gochfeld 2005; Ashraf 2006), canned tuna, and in other canned fish (Voegborlo et al. 1999; Burger and Gochfeld 2004; Khansari et al. 2005; Suppin et al. 2005; Taghipour and Azizi 2010; Boadi et al. 2011; Miklavčič et al. 2011; Mol 2011) have been reported to be below permissible limits in actual products available in the market (Mol 2011). In this study, the Hg concentration of all samples was below the permissible limits, i.e., even the more stringent 0.5 μg/g. Canned sardines and canned mackerel marketed in the USA and in Poland have been determined to be safe regarding this metal (Ikem and Egeibor 2005; Usydus et al. 2008). Likewise, concentrations of Hg in mackerel and sardines of Mediterranean regions were below the limits (Plessi et al. 2001; Falcó et al. 2006). However, it should not be ignored that many fish have developed a physiological mechanism of Hg detoxification. This mechanism involves the reaction of Hg with Se, which is an essential trace element (Flores-Arce 2007; Ralston et al. 2007). The protective effects of Se against Hg toxicity have been demonstrated in many animals and in humans (Falnoga and Tusek-Znidaric 2007; Kaneko and Ralston 2007). Therefore, Se concentration must also be considered when Hg concentration is high or above the limits.

It is known that the estimation of Sn in canned food is significant both for human health and quality assessment. A high Sn content indicates migration of Sn from the container to food usually because of poor lacquering (Sumitani et al. 1993; Tarley et al. 2001). The upper limit of Sn has been set as 250 μg/g (Mol 2011). In this study, the highest concentration of Sn was observed in canned Kilka (0.48 μg/g), which is far below the limit. Likewise, the concentration of Sn in canned fish has been found to be below the limit in various studies (Tarley et al. 2001; Ikem and Egeibor 2005). Because of the low Sn values observed, it might be concluded that there was no migration of Sn from the can to the fish. This is the result of new packaging technologies, especially the use of cans with lacquered walls and a mechanical seam (Khansari et al. 2005).

This study may help in generating data needed for surveillance programs aimed at ensuring the safety of the food supply and minimizing human exposure. It is hoped that monitoring of these metals regularly will increase the consumer confidence in canned fish products from Iran.

References

Ashraf, W. (2006). Levels of selected heavy metals in tuna fish. *Arabian Journal for Science and Engineering, 31*(1A), 89–92.

Ashraf, W., Seddigi, A., Abulkibash, A., & Khalid, M. (2006). Levels of selected metals in canned fish consumed in Kingdom of Saudi Arabia. *Environmental Monitoring and Assessment, 117*, 271–279.

ASTDR (1999). Toxicological profile for mercury, U.S. Department of Health and Human Service. Public Health Service, Agency for Toxic Substances and Disease Registry, Atlanta, p. 676

ASTDR (2003). Toxicological profile for selenium, Department of Health and Human Service. Public Health Service, Public Health Service, Agency for Toxic Substances and Disease Registry, Atlanta, p. 599

ASTDR (2005) Toxicological profile for tin, U.S. Department of Health and Human Service. Public Health Service, Public Health Service, Agency for Toxic Substances and Disease Registry, Atlanta, p. 426

Berry, M. J., & Ralston, N. V. C. (2008). Mercury toxicity and the mitigating role of selenium. *EcoHealth, 5*(4), 456–459.

Bhattacharyya, S., Chaudhuri, P., Dutta, S., & Chandra Santra, S. (2010). Assessment of total mercury level in fish collected from East Calcutta Wetlands and Titagarh sewage fed aquaculture in West Bengal, India. *Bulletin of Environmental Contamination and Toxicology, 84*, 618–622.

Boadi, N. O., Twumasi, S. K., Badu, M., & Osei, I. (2011). Heavy metal contamination in canned fish marketed in Ghana. *American Journal of Scientific and Industrial Research, 2*(6), 877–882.

Burger, J., & Gochfeld, M. (2004). Mercury in canned tuna: white versus light and temporal variation. *Environmental Research, 96*, 239–249.

Burger, J., & Gochfeld, M. (2005). Heavy metals in commercial fish in New Jersey. *Environmental Research, 99*(3), 403–412.

Environmental Protection Agency (EPA) (1998) Assessing human health risks from chemically contaminated fish and shellfish: a guidance manual. EPA-503/8-89-002, Appendix F. US Environmental Protection Agency, Cincinnati

Essig, D. A., & Kosterman, M. A. (2008). *Arsenic, mercury, and selenium in fish tissue from Idaho lakes and reservoirs: a statewide assessment*. Idaho: Idaho Department of Environmental Quality. 80.

E.U. (2005). Commission regulation as regards heavy metals. Amending Regulation 466/2001, no 78/2005.

Falcó, G., Llobet, J. M., Bocio, A., & Domingo, J. L. (2006). Daily intake of arsenic, cadmium, mercury, and lead by consumption of edible marine species. *Journal of Agricultural and Food Chemistry, 54*, 6106–6112.

Falnoga, I., & Tusek-Znidaric, M. (2007). Selenium–mercury interactions in man and animals. *Biological Trace Element Research, 119*(3), 212–220.

FDA (2001) Fish and fisheries products hazards and controls guidance. U.S. Food and Drug Administration, Center for Food Safety & Applied Nutrition, Chapter 9, Environmental chemical contaminants and pesticides, p. 26

Flores-Arce, M. F. (2007). Proceedings of the international symposium on selenium–mercury interactions. *Biological Trace Element Research, 119*(3), 193–194.

Food and Agricultural Organization of the United Nations and World Health Organization (FAO/WHO) (1984) List of maximum levels recommended for contaminations by the joint FAO/WHO Codex Alimentarius Commission, Second Series CAC/FAL, Rome, 3, 1–8

Food and Agricultural Organization of the United Nations and World Health Organization (FAO/WHO) (2009) Codex general standard for food additives, Codex standards, 192-1995, p. 259

Ghosh, N., & Bhattacharya, S. (1992). Thyrotoxicity of the chlorides of cadmium and mercury in rabbit. *Biomedical and Environmental Sciences, 5*, 236–240.

Ikem, A., & Egeibor, N. O. (2005). Assessment of trace elements in canned fishes (mackerel, tuna, salmon, sardines and herrings) marketed in Georgia and Alabama (United States of America). *Journal of Food Composition and Analysis, 18*, 771–787.

Kalay, M., Aly, O., & Canil, M. (1999). Heavy metal concentrations in fish tissues from the Northeast Mediterranean sea. *Bulletin of Environmental Contamination and Toxicology, 63*, 673–681.

Kaneko, J. J., & Ralston, N. V. C. (2007). Selenium and mercury in pelagic fish in the Central North Pacific near Hawaii. *Biological Trace Element Research, 119*(3), 242–254.

Khansari, F. E., Ghazi-Khansari, M., & Abdollahi, M. (2005). Heavy metals content of canned tuna fish. *Food Chemistry, 93*, 293–296.

Lourenço, H. M., Afonso, C., Martin, M. F., Lino, A. R., & Nunes, M. L. (2004). Levels of toxic metals in canned seafood. *Journal of Aquatic Food Product Technology, 13*(3), 117–125.

Miklavčič, A., Stibilj, V., Heath, E., Polak, T., Snoj Tratnik, J., Klavž, J., Mazej, D., & Horvat, M. (2011). Mercury, selenium, PCBs and fatty acids in fresh and canned fish available on the Slovenian market. *Food Chemistry, 124*(3), 711–720.

Mol, S. (2011). Levels of heavy metals in canned bonito, sardines, and mackerel produced in Turkey. *Biological Trace Element Research, 143*, 974–982.

Oehlenschläger, J. (2005). Identifying heavy metals in fish. In H. A. Bremner (Ed.), *Safety and quality issues in fish processing* (pp. 95–108). Cambridge: Woodhead and CRC.

Ordiano-Flores, A., Galván-Magaña, F., & Rosiles-Martínez, R. (2011). Bioaccumulation of mercury in muscle tissue of yellowfin tuna, *Thunnus albacares*, of the Eastern Pacific Ocean. *Biological Trace Element Research, 144*(1–3), 606–620.

Plessi, M., Berteli, D., & Monzani, A. (2001). Mercury and selenium content in selected seafood. *Journal of Food Composition and Analysis, 14*, 461–467.

Ralston, N. V. C., Blackwell, J. L., & Raymond, L. J. (2007). Importance of molar ratios in selenium-dependent protection against methylmercury toxicity. *Biological Trace Element Research, 119*(3), 255–268.

Raymond, L. J., & Ralston, N. V. C. (2004). Mercury: selenium interactions and health implications. *Seychelles Medical and Dental Journal, 7*(1), 72–77.

Rezayi, M., Esmaeli, A. S., & Valinasab, T. (2011). Mercury and selenium content in *Otolithes ruber*, and *Psettodes erumei* from Khuzestan Shore, Iran. *Bulletin of Environmental Contamination and Toxicology, 86*, 511–514.

Rose, J., Hutcheson, M. S., West, C. R., & Pancorbo, O. (1999). Fish mercury distribution in Massachusetts, USA lakes. *Environmental Toxicology and Chemistry, 18*(7), 1370–1379.

Ruelas-Inzunza, J., Meza-Lopez, G., & Paez-Osuna, F. (2008). Mercury in fish that are of dietary importance from the coasts of Sinaloa (SE Gulf of California). *Journal of Food Composition and Analysis, 21*(3), 211–218.

Sobhanardakani, S., Tayebi, L., & Farmany, A. (2011). Toxic metal (Pb, Hg and As) contamination of muscle, gill and liver tissues of *Otolithes rubber*, *Pampus argenteus*, *Parastromateus niger*, *Scomberomorus commerson* and *Onchorynchus mykiss*. *World Applied Sciences Journal, 14*(10), 1453–1456.

Sumitani, H., Suekane, S., Nakatani, A., & Tatsuka, K. (1993). Inductively-coupled plasma-atomic emission spectrometric determination of tin in canned food. *Journal of AOAC International, 76*, 1374–1377.

Suppin, D., Zahlbrucker, R., Krapfenbauer-Cermak, C. H., Hassan-Hauser, C. H., & Smulders, F. J. M. (2005). Mercury, lead and cadmium content of fresh and canned fish collected from Austrian retail operations. *Nutrition, 29*, 456–460.

Taghipour, V., & Azizi, S. N. (2010). Determination of trace elements in canned Kilka fish marketed in Islamic Republic of Iran. *World Applied Sciences Journal, 9*(6), 704–707.

Tansel Şireli U., Göncüoğlu1 M, Yıldırım Y, Gücükoğlu A, & Çakmak Ö (2006) Assessment of heavy metals (cadmium and lead) in vacuum packaged smoked fish species (mackerel, *Salmo salar* and *Oncorhynhus mykiss*) marketed in Ankara (Turkey). E.U. Journal of Fisheries and Aquatic Sciences, 23(3–4), 353–356.

Tariq, J., Ashraf, M., & Jaffar, M. (1993). Selected trace metals in fish, sediments and water from freshwater Tarbella reservoir, Pakistan. *Toxicological and Environmental Chemistry*, 39, 201–205.

Tarley, C. R. T., Coltro, W. K. T., Matsushita, M., & de Souza, N. E. (2001). Characteristic levels of some heavy metals from Brazilian canned sardines (*Sardinella brasiliensis*). *Journal of Food Composition and Analysis, 14*, 611–617.

Tayebi, L., Sobhanardakani, S., Farmany, A., & Cheraghi, M. (2011). Mercury content in edible part of *Otolithes ruber* marketed in Hamedan, Iran. International Conference on Environmental and Ecological Engineering, World Academy of Science, Engineering and Technology, Venice

Turkish Food Codex. (2002). Su Urunleri Yonetmeligi, Official Gazette, 9, No. 24936, Ankara, Turkey.

Turkmen, M., Turkmen, A., Tepe, Y., Tore, Y., & Ates, A. (2009). Determination of metals in fish species from Aegean and Mediterranean seas. *Food Chemistry, 113*, 233–237.

Underwood, E. J. (1977). *Trace elements in human and animal nutrition* (4th ed., p. 545). New York: Academic.

Usydus, Z., Szlinder-Richert, J., Polak-Juszczak, L., Kanderska, J., Adamczyk, M., Malesa-Ciecwierz, M., & Ruczynska, M. (2008). Food of marine origin: between benefits and potential risks. Part I, canned fish on the Polish market. *Food Chemistry, 111*(3), 556–563.

Voegborlo, R. B., El-Methnani, A. M., & Abedin, M. Z. (1999). Mercury, cadmium and lead content of canned tuna fish. *Food Chemistry, 67*, 341–345.

World Health Organization (WHO). (1996). *Guidelines for Drinking Water Quality. Vol. 2: health criteria other supporting information* (2nd ed., pp. 318–388). Geneva: WHO.