JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Effect of Processing Conditions on Trace Elements in Fish Roe from Six Commercial New Zealand Fish Species

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The concentrations of trace elements in fish roes and the effect of processing conditions (karasumi-like or karashi mentaiko) were investigated in six commercial fish species from New Zealand. The studied elements were As, Cd, Cr, Cu, Hg, Pb, and Zn, and the roes were from the following species: chinook salmon (*Oncorhynchus tshawytscha*), hoki (*Macruronus novaezelandiae*), southern blue whiting (*Micromesistius australis*), hake (*Merluccius australis*), blue warehou (*Seriolella brama*), and barracouta (*Thyrsites atun*). The concentrations of As, Cd, Cr, Hg, and Pb in the roes were lower than literature values for fish muscles. Only Zn in barracouta roe and Cu in salmon roe and their products were relatively higher than the generally accepted levels in fish muscles and could be of safety concern. Hence, the consumption of barracouta and salmon roes among certain parts of the population needs to be monitored and assessed. Dry salting (karasumi-like) processing increased ($P < 0.001$) the concentrations of the studied trace elements while salting fermentation (karashi mentaiko) processing tended to decrease the levels of trace elements. Fermentation may be a useful process to decrease the level of toxic trace elements.

KEYWORDS: Trace elements; fish roe; processing conditions; New Zealand

INTRODUCTION

Trace elements are found naturally at various levels in the hydrosphere, and many are required in minute amounts for physiological and metabolic processes of organisms (*1*). Trace elements are generally classified as either essential elements (e.g., Zn, Cu, and Fe) or toxic elements (e.g., Hg, Cd, and Pb). However, both deficiency and excess intake of essential elements can be detrimental to human health. As top predators, fish may be the end reservoir of the bioaccumulation of trace elements in a food chain, causing them to be potentially hazardous to consume (*2, 3*). With the constant increase in industrial activity, urbanization, geothermal activities, and natural disasters (e.g., earthquakes and tsunamis), the aquatic environment is destined for increased contamination, and consequently, higher contamination levels in fish can be expected. Trace elements accumulation in fish is dependent on numerous factors (*3*), and the accumulation pattern is the result of physiological uptake and elimination rates (*4*). Several reports have demonstrated the regulation of trace elements in fish (*5–8*) as well as the preferential accumulation in different organs of marine organisms (*2, 9–13*). Most of this research was focused on the distribution of trace elements in the muscle, liver, kidney, gills, and gut of marine species, but very little information is available on the trace elements status in fish roes (*6*).

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Fish roes are utilized mainly to produce caviar and caviar-like products in many parts around the world, and products such as salted-dried, salted-fermented, or salted-cured roes are found under traditional names in many countries. Although fish roe products are appreciated in many countries (Russia, Japan, Taiwan, parts of China, Korea, Greece, Italy, France, Spain, Scandinavian countries, Egypt, Lebanon, etc.) and consumers who have the taste for these products are loyal consumers with regular consumption habits, there are very few reports that have been published on the trace elements in these products (*14*). Therefore, this study aims to investigate the concentrations of seven essential and toxic elements (As, Cd, Cr, Cu, Hg, Pb, and Zn) in the raw roes of six commercial fish species and to study the effects of processing conditions [salted-dried ("karasumi-like") and salted-fermented ("karashi mentaiko") at room temperature or in a chiller at 5 °C] on the levels of these trace elements in the final products.

MATERIALS AND METHODS

Sample Collection. Chinook salmon (*Oncorhynchus tshawytscha*), hoki (*Macruronus novaezelandiae*), southern blue whiting (SBW) (*Micromesistius australis*), hake (*Merluccius australis*), blue warehou (*Seriolella brama*), and barracouta (*Thyrsites atun*) roes (grade 1 or 2; each sample was between 20−40 kg) were supplied from commercial production establishments in New Zealand. The grades correspond to the classification scheme used in commercial plants and refer to the intactness and the absence of visible blood vessels on the roe surface. The samples were received either frozen (hoki, SBW, mature salmon, hake, and warehou) or fresh (barracouta and immature salmon). Sam-

10.1021/jf8005646 CCC: $40.75
Published on Web 05/22/2008

Table 1. Concentrations of Trace Elements (mg/kg Wet Weight) in Raw Fish Roes from Some Commercial Fish Species in New Zealand[a]

species	As	Cd	Cr	Cu	Hg	Pb	Zn
barracouta	0.61 b	0.021 c	<0.05	1.03 a	0.029 ab	<0.002	108.00 d
hake	0.80 b	0.005 a	<0.05	0.66 a	0.034 b	<0.002	41.25 ab
hoki	0.55 b	0.002 a	<0.05	1.00 a	0.012 ab	<0.002	32.20 a
salmon (mature)	0.11 a	0.002 a	<0.05	2.61 b	0.029 ab	<0.002	37.80 ab
SBW	1.86 c	0.002 a	<0.05	0.74 a	0.008 a	<0.002	25.00 a
salmon (immature)	0.09 a	0.002 a	<0.05	6.20 c	0.017 ab	<0.002	60.70 c
warehou	2.00 c	0.012 b	<0.05	1.02 a	0.010 a	<0.002	55.50 bc
DORM 2 (dogfish muscle)	18.10	0.044	34.1	1.96	4.43	0.062	24.8
experimentally obtained value	18.0 ± 1.1	0.043 ± 0.008	34.7 ± 5.5	2.34 ± 0.16	4.64 ± 0.26	0.065 ± 0.007	25.6 ± 0.32
recovery (%)	100.6	101.6	98.3	83.8	95.5	95.4	96.9
limits of detection	0.02	0.0004	0.05	0.01	0.002	0.002	0.02

[a] Roe values within columns with different letters are significantly different ($P < 0.01$).

ples were kept frozen at −20 °C and thawed at 5 °C overnight when required for processing. The catch data, maturity index, and fish size were unavailable for the species. Only whole (undamaged) roe skeins were used for analysis and processing.

Processing of Samples. *Salted-Dried (Karasumi, Bottarga, and Batarekh).* Salted-dried products were prepared according to the method for karasumi (*15*). Thawed roes were covered with salt (10% of the roe weight) and kept in the chiller at 5 °C for 12 (barracouda, immature salmon, and SBW) or 24 h (hoki, hake, and warahou) depending on the size of the roes. At the end of the salting step, the roes were washed thoroughly in ice-cold water and drained for 1 h. The roes were pressed under weights and then spread in a single layer over Teflon-coated mesh trays, air-dried at room temperature (≅21 °C), and turned daily until the desired texture was achieved. A repeat pressing under weights was carried out when required.

Salted-Cured (Sujiko). The hako-kiri brining method (*15*) was used to produce sujiko from immature salmon roes only.

Salted and Fermented Products (Kara-shi-mentaiko and Jeotgal). Thawed roes were individually mixed with 7% (of the raw weight) salt and 5% chili and vacuum packed. The mixtures were stored in a dark, cool place at room temperature or at 5 °C for 4 weeks.

Analysis of Trace Elements in Fish Roes. A 2.5 g sample of fresh roe, weighed accurately to three decimal places, was placed in 50 mL graduated polycarbonate tubes, and 2.5 mL of nitric acid and 0.5 mL of hydrochloric acid were added. The tubes were capped and digested for 60 min in a 90 °C heating block. The digested samples were cooled and diluted to 50 mL with deionized water. Trace elements in the diluted digests (As, Cd, Cr, Cu, Hg, Pb, and Zn) were analyzed by inductively coupled plasma−mass spectrometry using a Perkin-Elmer Elan 6000 instrument. These trace elements were chosen because they are the most widely reported in the literature on fish roe and for the benefit of comparison. The calibrating standards were prepared as "multielement" solutions using BDH Spectrosol Standards and were diluted in a solution of 5% (v/v) nitric acid/1% (v/v) hydrochloric acid to match the acid matrix of the diluted sample digests. Certified reference material (NRCC-DORM-2 Dogfish Muscle) was analyzed for corresponding elements to validate the method for accuracy and precision. The limits of detection for As, Cd, Cr, Cu, Hg, Pb, and Zn were 0.02, 0.0004, 0.05, 0.01, 0.002, 0.002, and 0.02 mg/kg, respectively.

Data Analysis. Analysis of variance was used to test for fish species and processing effects on the mean concentration of trace elements. The data were analyzed using the general linear model protocol in MINITAB (release 14.1). For species and processing effects within species, the significance of the difference between means was determined by Tukey's multiple comparison test ($P < 0.01$). Samples were analyzed in duplicate, and the means were for three samples per treatment × species combination.

RESULTS AND DISCUSSION

Trace Elements in Raw and Processed Fish Roes. The concentrations of trace elements in salted-cured (sujiko) were not different from immature salmon roes; thus, it will not be considered in the following discussion to avoid repetition.

Lead. Pb concentrations in fresh roe were below the detection limit of 0.002 mg Pb/kg fresh roe in all species (**Table 1**). Pb concentrations in fish roes in the present study were much lower than the Pb concentrations reported for either whole fish or fish muscle from New Zealand (*10, 16, 17*), Australia (*7, 18*), and the Mediterranean sea (*11*). Several studies have demonstrated that metal levels vary in different parts of fish (e.g., flesh, guts, and gills) and among different species (*2, 6, 9, 10, 13*). In general, Pb levels were found in the following order: gill > liver (viscera) > flesh (*2, 9, 10, 13*), which can be explained by selective accumulation of the metal in gills, liver, and kidneys as compared with muscle tissues (*19, 20*). The Pb concentration of less than 0.002 mg Pb/kg fresh roe is far below the 0.5 mg/kg maximum level recommended by Food Standards Australia and New Zealand (*21*). The provisional tolerable daily intake of 0.215 mg Pb/day for a 60 kg adult (*22*) would require the consumption of more than 100 kg of fresh roe.

The Pb concentration values of raw roe could not be compared statistically with their products because of the detection limit (**Table 2**). However, a numerical increase in Pb concentrations was observed in the processed samples, which were dependent on the fish species. For example, an increase in Pb concentrations in karasumi-like and karashi mentaiko produced at room temperature was found in barracouta (at least 12- and 3-fold, respectively) and hake roes (2.5-fold for both) as compared with raw roes and karashi mentaiko produced in the chiller, whereas an increase in hoki and salmon Pb concentrations occurred only in karashi mentaiko produced in the chiller. Also, an increase in Pb concentrations was found in karasumi and karashi mentaiko produced in the chiller in SBW and warehou roes. However, none of the changes during the salting-drying process increased Pb to unsafe levels.

Chromium. Cr concentrations in fresh roe were below the detection limit (<0.05 mg/kg) and were well below the level of concern (13 mg/kg) reported by the U.S. Food and Drug Administration for chronic seafood consumers (*23*). Cr is not listed in FSANZ standards for seafood probably because inhalation is the main route for carcinogenicity by the hexavalent form (+6) (*24*) and most of the Cr available in biota is in the less toxic trivalent (+3) form (*23*). Furthermore, the (+6) form of Cr is reduced to the (+3) form in the gastric system (*25, 26*), making the potential of toxicity of the (+6) form even less through the digestive tract. In comparison, Cr concentrations in fish roe in the present study are far lower than the Cr contents found in fish muscle from New Zealand waters (range, 0.12−0.92 mg/kg wet wt) (*10, 27*), Australia (range, 0.44−0.63 mg/kg dry wt), Mediterranean (range, 1.24−17.1 mg/kg dry wt), and California (range, 0.27−3.0 mg/kg dry wt) (*28*). This does not necessarily

Table 2. Changes in the Concentrations of Trace Elements (mg/kg Wet Weight) during the Processing of Fish Roes from Some Commercial Fish Species in New Zealand[a]

species	material		storage	As	Cd	Cr	Cu	Hg	Pb	Zn
barracouta	raw			0.61 a	0.021 ab	<0.05	1.03 b	0.029	<0.002	108.00 b
	processed	karashi mentaiko	chiller	0.61 a	0.017 a	<0.05	0.98 ab	0.030	<0.002	76.75 a
			room	0.50 a	0.013 a	<0.05	0.86 a	0.021	0.006	71.80 a
		karasumi-like		1.12 b	0.033 b	<0.05	2.03 c	0.069	0.024	199.00 c
hake	raw			0.80	0.005 a	<0.05	0.66 a	0.034	<0.002	41.25 a
	processed	karashi mentaiko	chiller	1.22	0.013 ab	<0.05	0.65 a	0.033	<0.002	36.50 a
			room	0.69	0.013 ab	<0.05	0.63 a	0.029	0.005	33.30 a
		karasumi-like		1.72	0.024 b	0.06	1.09 b	0.090	0.005	66.75 b
hoki	raw			0.55 a	0.002	<0.05	1.00 ab	0.012 a	<0.002	32.20 b
	processed	karashi mentaiko	chiller	0.49 a	0.002	<0.05	0.81 a	0.020 ab	0.003	26.10 ab
			room	1.27 c	0.002	<0.05	0.78 a	0.010 a	<0.002	21.70 a
		karasumi-like		0.88 b	0.003	<0.05	1.47 b	0.030 b	<0.002	50.20 c
salmon (mature)	raw			0.11 a	0.002 a	<0.05	2.61 a	0.029	<0.002	37.80 a
	processed	karashi mentaiko	chiller	0.12 a	0.002 a	<0.05	1.75 a	0.020	0.004	22.70 a
			room	0.41 b	0.002 a	<0.05	1.01 a	0.023	<0.002	50.50 a
		karasumi-like		0.35 b	0.005 b	<0.05	12.95 b	0.024	<0.002	118.50 b
SBW	raw			1.86 a	0.002 a	<0.05	0.74 a	0.008 a	<0.002	25.00 b
	processed	karashi mentaiko	chiller	1.99 a	0.003 b	<0.05	0.65 a	0.008 a	0.004	18.20 a
			room	1.50 a	0.003 b	<0.05	0.59 a	0.010 a	<0.002	17.20 a
		karasumi-like		4.09 b	0.005 c	<0.05	1.14 b	0.013 b	0.007	38.00 c
salmon (immature)	raw			0.09	0.002	<0.05	6.20 a	0.017 a	<0.002	60.70 ab
	processed	karashi mentaiko	chiller	0.09	0.002	<0.05	4.08 a	0.017 a	0.005	29.90 a
			room	0.12	0.003	<0.05	5.94 a	0.013 a	0.006	50.00 ab
		karasumi-like sujiko		0.15	0.002	<0.05	14.99 b	0.059 b	<0.002	67.30 b
				0.10	0.002	<0.05	5.01 a	0.010 a	<0.002	21.90 a
warehou	raw			2.00	0.012 ab	<0.05	1.02 ab	0.010	<0.002	55.50 a
	processed	karashi mentaiko	chiller	2.03	0.016 bc	<0.05	0.83 a	0.014	0.005	49.40 a
			room	2.02	0.011 a	<0.05	1.04 ab	0.011	<0.002	49.60 a
		karasumi-like		2.41	0.019 c	<0.05	1.40 b	0.018	0.005	73.30 b

[a] Values within each species with different letters are significantly different ($P < 0.01$).

means that roe has a lower Cr content than muscles since Cr contents were <1, <0.8−0.57, and <1.2 mg/kg dry wt for Cod muscle, liver, and ovaries, respectively (*6*). No major effects were found for processing conditions or species on Cr concentrations in raw and processed roe products (**Table 2**).

Zinc. A wide variation in Zn concentrations was found among raw roe from different species ($P = 0.002$). Barracouta roe had 2.5−4 times higher Zn concentrations than roe from hake, hoki, SBW, and mature salmon (**Table 1**). Immature salmon had nearly twice the Zn concentration that was available in mature salmon. The present results suggest that immature roes (barracouta and salmon) contain higher concentrations of Zn than mature roes. This is in agreement with an earlier observation that juvenile cod roe had three times more Zn than mature cod roe (*29*) (cited in ref *20*). However, environmental factors also seem to influence the amount of Zn in fish and shellfish. For instance, the Zn concentration in roe from the Northwest Atlantic cod (*6*) was 2−4 times higher than from Northern Norway cod (*29*), and oysters from the Atlantic had 8−9 times the concentration of Zn in oysters from the Pacific (*30*). The amount of Zn in barracouta's roe in the present study (333.8 mg/kg dry wt) is similar to the range (290−421 mg/kg dry wt) reported for cod roe from Northwest Atlantic (*6*).

While there is no maximum level specified for Zn in the Australia New Zealand Food Standards Code for fish and seafood, a generally accepted level is 5 mg/kg of fish or 25 mg/kg of certain seafood (e.g., lobster) (*21*). The recommended daily allowance (RDI) of Zn is 10 and 15 mg/day in children and adults, respectively (*31*). A more recent lower RDI (8.76 and 10.92 mg/day, based on 60 kg body weight for adult males and females, respectively, and 7.35 and 6.93 mg/day based on 30 kg body weight for boys and girls, respectively) are in place for New Zealand and Australia (*21*). These figures suggest that depending on the fish species, only between 100 and 500 g of roe per day could be required from the studied species to achieve the RDI of Zn. Regarding the toxic level of Zn, a 45 mg/day limit was recommended by the World Health Organization in 1996 as the maximum tolerable limit for the adult population (*22*), which correspond to 400−2000 g of roes, which is unlikely to be the serving size for normal meals.

Karasumi-like products from barracouta, hake, hoki, SBW, and warehou had Zn concentrations 1.5−2 times higher than raw roe ($P < 0.05$) (**Table 2**). While the Zn content in mature salmon roe increased more than 3-fold as a result of karasumi-like processing, no change in the Zn content was found in immature salmon roe after the same processing. This probably reflects differences in Zn availability and the binding capacity of biochemical compounds required differently at immature and mature stages of egg development, as distinct protein profiles for eggs have been found in our samples (data not shown) and differences in the biochemical network have been reported at different development stages (*32, 33*). Karashi mentaiko processing tended to cause a decrease in Zn concentrations, which was significant in barracouta and SBW and in hoki processed at room temperature only. No differences were found in Zn concentrations in karashi mentaiko produced at room temperature or in a chiller. Overall mean effects of processing conditions on trace elements (**Figure 1**) revealed an increase in Zn content with karasumi-like production and a tendency toward reduction in karashi mentaiko processing. The salting-drying process reduced the moisture content and thus increased the metal concentration. The reduction in karashi mentaiko can be explained by leaching into the drip accumulated during the curing/ripening step as a result of the protein degradation and moisture migration out of the roes. The moisture withdrawal and salt migration process tended to be greater at room

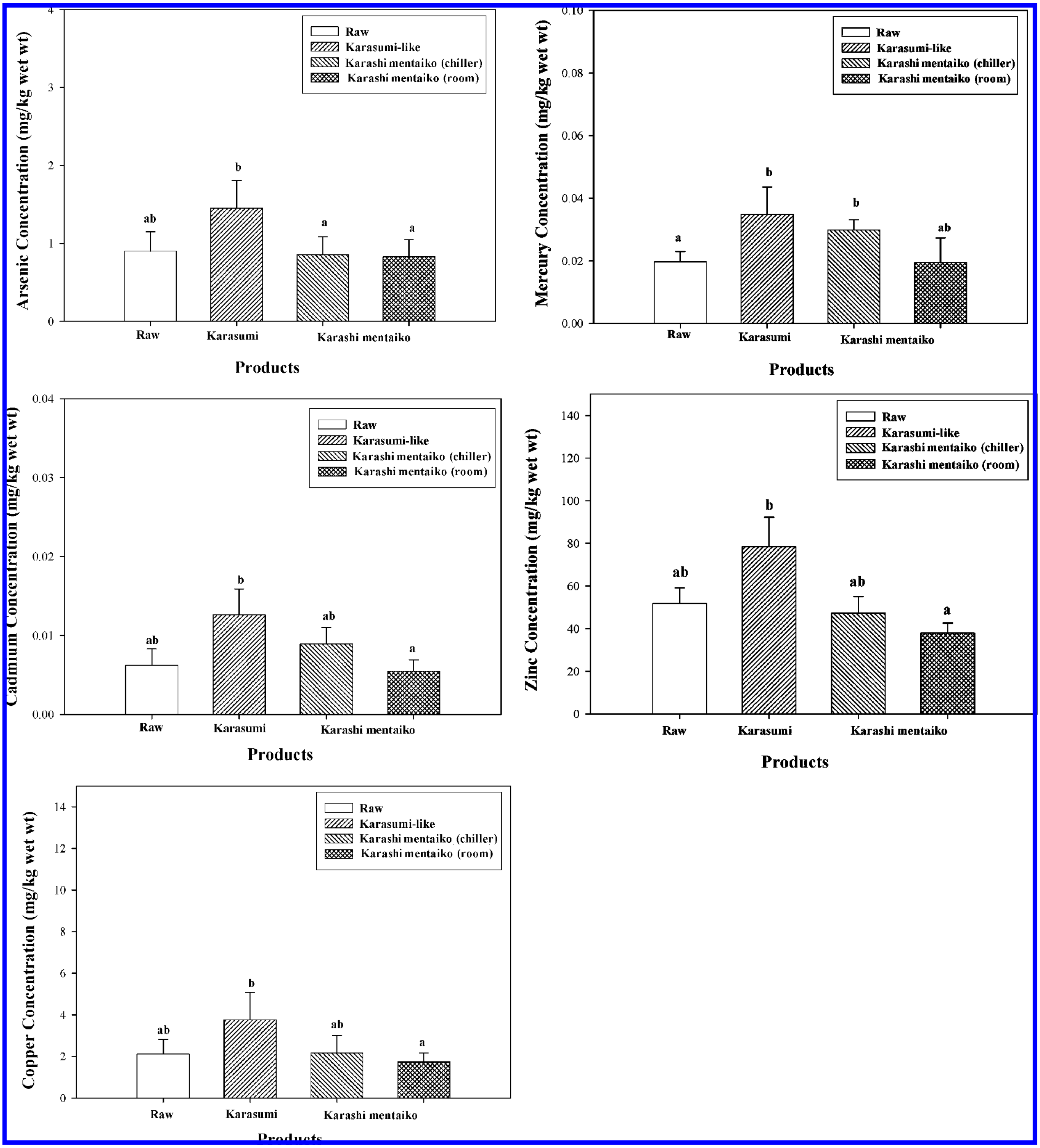

Figure 1. Main effects of processing conditions on trace element concentrations in fish roe.

temperature than at the chiller temperature, as revealed by the higher total ash and lower moisture contents (data are not shown).

All karasumi-like products, except for SBW, had a higher Zn content (50.2−199 mg/kg wet wt) than the salted-dried hake reported by Rodrigo et al. (*14*). Only karasumi-like products from barracouta and mature salmon had higher Zn contents than salted-dried roes from ling (*14*) and mullet (*20*). In fact, the Zn contents in karasumi-like products from barracouta were very high (199 mg/kg wet wt) as compared with any other roe products reported in the literature. For example, salted-dried mullet, hake, and ling were reported to have Zn contents of about 100, 41, and 110 mg/kg wet wt, respectively (*14, 20*), and caviar from different sturgeon species and locations had a range between 10.3−12 mg/kg wet wt (*34*) and 23.2−26.4 mg/kg wet wt for Persian caviar (*35*). The average Zn content in karasumi-like products from hake in the present study (66 mg/kg wet wt) was 1.5 times that reported by Rodrigo et al. (*14*), which highlights the variation of trace element content within the same fish species in a different ecosystem. There were no safety concerns associated with karashi mentaiko processing, whereas karasumi processing might limit the maximum amount that can be consumed to 200 g (*36*).

Copper. Cu in the roe ranged between 0.66 and 6.20 mg/kg with the concentration in salmon roe about 2.5−6 times that of other species (**Table 1**). Immature salmon roe had significantly ($P < 0.01$) more Cu than mature salmon roe and the other studied species. The Cu concentrations in the studied roes are of intermediate values between those recently reported for several fish muscles (0.12−0.3 g/g wet wt) and seafood such as abalone and lobsters (2.6−8.1 mg/kg wet wt) from the Victoria coast in Australia (*7*). Cu concentrations in mullet roe (2.3 mg/kg dry wt), cod roe (2.07−5.5 mg/kg dry wt), and catfish roe (0.086 mg/kg wet wt) suggested a wide variation among different fish species (*6, 20, 29, 37*). However, several reports found high biological variation in Cu concentrations in fish muscles within the same fish species whereas Cu concentrations among different species caught from the same area were not that different (*18, 38, 39*). This probably suggests that environmental and physical factors (e.g., age and size) may play a major role in the accumulation of trace elements, and probably, this can explain the marked differences between the salmon roes and the other species in the present study.

Cu is involved in many important metalloenzymes (for a review, see ref *40*), and both excess and deficiency can lead to diseases. The toxic limit of Cu is 30 mg/kg (*41*). There is no clear maximum level for Cu in food; however, the acceptable range of oral intake is believed to be in the range of several but not many (stated more than 2−3 mg/day) mg/day for adults (*42*). The generally accepted levels for Cu are 0.5, 5, and 10 mg/kg for fish, abalone, and lobster, respectively (*7, 21*). Only immature salmon roes might be of concern if consumed in large quantities (>1 kg/day).

Karasumi-like products from barrcouta, hake, SBW, and mature and immature salmon had higher Cu concentrations as compared with raw roe. A 40−100% increase in Cu content was observed in karasumi-like products from barracouta, hake, hoki, SBW, and warehou roe as compared with raw roe (**Table 2**). An increase of 2- and 5-fold was found in karasumi-like products from immature and mature salmon roe, respectively, as compared with raw roe. Cu concentrations in karasumi-like products were higher than karashi mentaiko products except for warhou processed at room temperature ($P < 0.05$). Generally speaking, Cu concentrations in karashi mentaiko products were not different from raw roe (except for barracouta processed at room temperature), and the temperature had no effect on the Cu concentration. The mean effects of processing conditions show the expected increase in Cu concentrations with karasumi-like product and slightly lower Cu contents of karashi mentaiko processed at room temperature (**Figure 1**). All processed products, except those from salmon, had Cu levels less than those reported for salted-dried hake and ling (2.5 and 6.6 mg/kg wet wt, respectively) (*14*) and sturgeon caviar (range, 1.2−1.69 mg/kg wet wt) (*34, 35*).

All processed products will contain Cu levels that are higher than the generally accepted level for fish (0.5 mg/kg wet wt) but lower than those existing for seafood (5 and 10 mg/kg wet wt for abalone and lobster, respectively), except karasumi-like products from salmon. Karasumi-like products from immature and mature salmon had Cu levels that were 30−50% of the toxic limit of 30 mg/kg for Cu set by the FAO (*41*), and this may be of concern.

Arsenic. Total As concentrations in marine fish roes (barracouta, hake, hoki, SBW, and warehou) were higher than freshwater roes (salmon). It is well-known that marine organisms have a great tendency to bioaccumulate As (*43*). The provisional total daily intake is 0.002 mg (inorganic As)/kg body weight (*43, 44*). There is no listing for total As concentrations in fish and crustacea in the Food Standards Australia New Zealand, but there is a maximum limit (ML) of 2 mg (inorganic As)/kg for fish and crustacea (*21*). None of the roe in the present study imposed a health hazard since less than 5% of the total As in fish and crustacea are found in the inorganic form (*7, 45*), which will result in an inorganic As level well below the ML of 2 mg/kg.

Karasumi-like products from barracouta, hoki, mature salmon, and SBW had a 50−300% increase in As concentration as compared with their respective raw roe. Karashi mentaiko produced at room temperature from hoki exhibited a higher As content than the other treatments and raw roe. Similarly, karashi mentaiko produced at room temperature from mature salmon roe contained higher As concentration than raw roe and karashi mentaiko produced in a chiller ($P < 0.05$). Mean effects of processing conditions confirmed the expected increase in As content as a result of drying (**Figure 1**). While a high concentration of total As was found in SBW and warehou karasumi-like products (range, 1.5−4.1 mg/kg wet wt), these products are probably not a toxic hazard as the inorganic As will be in the range of 0.075−0.2 mg/kg wet wt (assuming that 5% of the total As is in the inorganic form).

Mercury. Fish consumption is the main source of dietary Hg intake (*46*). Frequent consumption of seafood can increase the percentage acquired through diet (*47*) and multiply the Hg levels as compared to a reference population (*48*). Total Hg contents in barracouta, hoki, and salmon roe were similar to hake, SBW, and warehou. Total Hg in the present study ranged between 0.008 and 0.034 mg/kg of roe and was the same range as that reported for mullet roe (0.021 mg/kg wet wt) (*20*), cod roe (0.015−0.018 mg/kg wet wt) (*6, 28*), and Alaska pollock (*Theragra chalcogramma*) roes from Russia (<0.01 mg/kg wet wt) but are 15 times lower than the Hg concentration found in alfonsino (*Beryx splendens*) roe from Japanese waters (0.49 ± 0.26 mg/kg wet wt) (*47*). While both Alaska Pollock and alfonsino share the same feeding habits (feed mainly on small fish, crustaceans, and cephalopods), they have significantly different levels of Hg, underpinning the importance of species and ecosystem in the bioaccumulation of Hg in marine organisms.

The level of Hg in different parts of the fish was reported to be in the following order: liver ≫ muscle > eggs in Canadian whitefish, pike, and lake trout (*49*). Fish muscle had higher Hg concentration than eggs in striped bass (*Morone saxatilis*) from the United States (*50*) and in alfonsino (*Beryx splendens*) from Japan (*47*). However, several factors such as location, fish length/age, season, or species might affect the accumulation pattern since in bream the accumulation of Hg was not different in muscle and liver (*51*). The ML for total Hg in fish and fish products is 0.5 mg/kg wet wt (*52*) for crustacea and fish except predator species (e.g., sharks, swordfish, billfish, and orange roughy) where the ML is 1 mg/kg wet wt (*21, 53*) . According to these data, none of the roe will be of safety concerns. In fact, the available data on the Hg concentrations in fish muscles and roes overseas (*6, 47*) and on fish from New Zealand (*17, 54, 55*) suggest that roes contain less Hg than fish flesh and thus are less likely to cause Hg toxicity as compared with fish muscles. Most of Hg in seafood is found in the organic form with 50−100% of total Hg having been reported as methylmercury in various types of fish from different locations (*18, 47, 54, 56*). The latest provisional tolerable weekly intake of methylmercury is 0.0016 mg/kg body wt (*57*), which means that a 60 kg adult could safely eat 3 kg of hake roes a week, even if all of the Hg is in the methylated form.

Karasumi-like products from hoki, SBW, and immature salmon had higher Hg concentrations as compared with karashi mentaiko products and raw roes from these species. No differences were found in Hg concentrations in karashi mentaiko produced at room temperature and in a chiller.

The overall effects of processing conditions on Hg concentrations in processed products as compared with raw roes are shown in **Figure 1**. Total Hg increased with processing ($P < 0.001$), but the increase was not different in karashi mentaiko processed at room temperature as compared with raw roes (**Figure 1**). The level of tolerable intake in karashi mentaiko will remain the same as the raw roes mentioned above; however, a 2−3-fold increase in Hg content of karasumi-like product from barracouta, hoki, hake, and mature salmon means that the allowable intake will be reduced as compared with the raw roe.

Cadmium. Barracouta roe had the highest Cd concentration followed by warehou roe, and no significant differences were found among hake, hoki, salmon, and SBW (**Table 1**). The concentrations of Cd in the present study are similar to those reported for mullet and cod roe (*6, 29*). The average reported Cd concentrations in fish muscle from Australasian water are 10−100-fold more than the concentrations found in the roe (except barrcouta and warehou) in the present study (*7, 10, 18, 38, 39*). Similar values were reported for fish from other parts of the world (*11, 13, 28, 51, 58–60*) except for fish from Canadian waters, which had comparable concentrations of Cd (*49*). The Cd concentrations were found to be in the following order: gill = liver > muscle (*11, 13, 51*). Higher (*6*) or mixed results (*49*) were reported for Cd concentrations in fish roes as compared with the fish muscle depending on the fish species and catch location. In less industrialized areas, no differences were found in Cd concentrations of different fish tissues (*60, 61*). There is no ML provision for Cd in fish or fish roe in the FSANZ standards; however, a 2 mg/kg fresh wt of molluscs (excluding oyster and queen scallops) is provided (*21*). A lower limit for crustaceans and bivalve molluscs (0.5 and 1 mg Cd/kg fresh wt, respectively) is set by the European Union (*53*). The Cd concentrations in the roes comply with both provisional limits. Furthermore, a latest provisional tolerable weekly intake of 0.007 mg Cd /kg body wt recommended by the FAO/WHO (*62*) means that the daily consumption of about 30 kg of hake, hoki, salmon, or SBW roe, 3 kg of barracouta roes, or 5 kg of warehou roes will comply with this provision. The slightly high Cd concentrations in barracouta and warehou roe are not a concern since these roe also contain a high Zn concentration, which has been suggested to counteract the absorption of Cd in the body (*63*).

Cd concentrations tended to increase in karasumi-like products, but only those from hake, mature salmon, SBW, and warehou had significantly higher Cd concentrations ($P < 0.05$) as compared with raw roes (**Table 2**). Mean effects of processing conditions showed that karsumi products, and to a lesser extent karashi mentaiko processed in a chiller, tended to have higher Cd concentrations whereas karashi mentaiko processed at room temperature tended to have lower Cd concentrations as compared with their raw materials. The Cd levels in all samples in the present work are lower than the <0.07 mg/kg wet wt reported for salted-dried mullet roe (*20*) but fall within the range reported for sturgeon caviar (range, <0.005 to <0.011 mg/kg wet wt). The latest provisional tolerable weekly intake of 0.007 mg Cd/kg body wt recommended by the FAO/WHO (*62*) means that the daily consumption of about 1.8 kg of karasumi-like product from barracouta, the product containing the highest Cd concentration, will comply with this provision.

A negative correlation ($P < 0.05$) between Cu and As and positive correlation ($P < 0.01$) between Zn and Cd concentrations has been found in raw fish roe (**Table 3**). These correlations were further confirmed for all treatments with higher *P* values. Further positive correlations between Zn and Cu, Zn and Hg, and Hg and Cd were found for all treatments (**Table 3**). This is in agreement with the positive correlations between Zn and Cd and Hg and Cd that have been reported for shark muscles (*39*) and in certain organs of cattle (*64*). Associations between these elements may reflect the biochemical regulation of element concentration or a requirement of elements (such as Zn and Cu) for the synthesis of detoxifying proteins enzymes (e.g., glutathione and dismutases) as a feedback mechanism for an increase in toxic elements (*8, 65*).

Table 3. Inter-relationship between Trace Elements (As Estimated by Pearson Correlation Values) in Raw and Processed Fish Roe from Barracouta, Hake, Hoki, Salmon (Mature and Immature), SBW, and Warehou in New Zealand[a]

	Zn	Cu	As	Hg
		Raw Material		
Cu	0.185			
As	−0.179	−0.629**		
Hg	0.202	−0.097	−0.485**	
Cd	0.806***	−0.373	0.335	0.085
		All Treatments		
Cu	0.329*			
As	−0.047	−0.401***		
Hg	0.420***	0.31**	−0.125	
Cd	0.622***	0.148	0.205	0.710***

[a] *$P < 0.05$, **$P < 0.01$, and ***$P < 0.001$.

The trace elements that are considered to be of most concern in New Zealand are As, Cd, Hg, and Pb. These contaminants are released into the environment from natural processes and human activities. Fish and shellfish are particularly susceptible to absorb and accumulate trace elements such as Pb, Cd, Cr, Cu, Hg, Zn, and Fe due to their feeding regime and behavior. Of particular importance is the availability of Hg in fish as methylmercury due to bacterial conversion in the marine environment. The variation in the metal concentrations in the raw roes studied may be explained by several factors including the feeding behavior of the fish. Fish that prey on molluscs and crustaceans have higher levels of trace elements in their bodies (*5*). In addition to the feeding regime, it has been shown that trace elements accumulate differentially in different fish organs (*9–11*) and that the accumulation pattern is greatly influenced by the ecosystem, fish species (*2, 12*), and element under investigation (*13*). Also, the fish activity (pelagic or rearing near the sediment bed of the water system), environment contamination gradients, salinity, and temperature can all influence the uptake of metals (*5, 13, 66*). The accumulation of Hg and Cd has been reported to correlate to the size of the fish (*47, 51, 67*), which might also contribute to the variation observed among and within species.

Specific bioaccumulation to organs has been reported with Hg tending to accumulate in higher concentrations in muscles, Cd and Zn in kidney, and Cu in liver (*68*). Similar tendencies have been confirmed in other reports (*60*) with fish eggs containing the highest Zn concentrations among all fish tissues. With regard to trace elements, roe may be considered a safer food than fish flesh because Cr and Hg concentrations were lower in roe (*50*). It has been suggested that essential metals such as Fe, Mn, Zn, and Cu are easily transferred from the mother to eggs, whereas levels of toxic metals such as Cd and Hg are transferred in limited amounts (*69*). This may reflect the regulatory nature of some essential elements within some fish species (*6, 7*) and highlight their biological importance as essential elements for enzymes and metalloproteins needed during ova development (*6*). This line of explanation is plausible since Julsham et al. (*29*) reported that essential trace elements were higher in the cod eggs as compared to the fish fillet (muscle) by a factor of 14, 6, 4, and 2 for Zn, Mn, Fe, and Cu, respectively, whereas levels of toxic metals were slightly lower in eggs than the fish muscle. Similar observations were reported for the eggs of *Syngnathus rostellatus*, which contained less Pb and especially less Cd and more Zn and Cu than the muscles of fish (*70*) and confirmed by Romeo (*20*) for mullet roe.

The concentration of trace elements was lower in fish roe and their products than that reported for fish muscle from New Zealand and overseas, apart from the high Zn in baracoutta roe and Cu content in salmon roe. Thus, it may be concluded that, with regard to the toxicity of the studied elements, fish roes are safer to consume than fish muscle.

This study showed the tendency of karashi metaiko processing to decrease the trace element concentration, which probably reflects their partitioning between the solid and the liquid phases. Thus, fermentation may provide a cheap decontamination technique where contamination and scarcity of food coexist, given that the solid (e.g., karashi mentaiko) is used separately from the drained liquid.

In New Zealand, fish roe consumption is higher among certain parts of the population (Maori, Asian, Polynesian, and Middle Eastern groups). Thus, the intake of fish roe in these groups needs to be monitored and assessed since Zn and Cu levels may be of concern. This research also shows that any processing (e.g., dry salting or cold smoking) or dry cooking (e.g., frying and roasting) that results in decreased moisture content may increase the risk of intake of trace elements especially with salmon and barracouta roes. Decontamination techniques and awareness of cooking consequences may be required for safe utilization of roe from certain species.

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Received for review February 25, 2008. Accepted April 8, 2008.

JF8005646