The available utilization of selenium from some inedible tissues of marine products-I: The distribution of selenium in several species of cultured and wild fish

Norihisa Kai (Department of Food Science and Technology, National Fisheries University, norikai@fish-u.ac.jp) Yasuhiro Tanoue (Department of Food Science and Technology, National Fisheries University, tanoue@fish-u.ac.jp) Yukinori Takahashi (Department of Applied Aqua-biology, National Fisheries University, takahashy@fish-u.ac.jp) Takeshi Nagai (Faculty of Agriculture, Yamagata University, tnagai@tds1.tr.yamagata-u.ac.jp)

Abstract

The selenium distribution in the scales or skin as one of the inedible tissues of several species of fish (Yellow tail *Seriora quinqueradiata*, Red sea bream *Pagrus major* and Puffer *Takihugu rubripes*) was investigated in order to clarify the possibility of the utilization of selenium from those discarded tissues, in relation with the mercury distribution involving tissue. Both distributions were compared with those of the ordinary muscle. As a result, each selenium level in the scales or skin was about the same or somewhat higher than that involving muscle between those cultured and wild species of subjected fish in the present study. On the other hand, the mercury level was extremely low or nearly zero and Se/Hg (the molar ratio of selenium to mercury) was drastically high compared with that involving muscle, suggesting that the scales or skin will be usually inedible but significantly safe tissue which few heavy metals such as mercury will tend to accumulate. These findings suggested that the available utilization of selenium may be expected from the scales or skin of fish, including the improvement of environment.

Key words

selenium, mercury, distribution, scale, available utilization

1. Introduction

Previous research has already reported the profiles of mercury distribution in the ordinary muscle of cultured olive flounder, red sea bream, amberjack and Japanese scad, in relation to those of selenium distribution (Kai et al., 2007; 2008; 2009; 2010; 2011; 2012). On the other hand, the mercury distribution in the scales of a few species was also investigated, but surprisingly little mercury accumulation was observed in involving submitted fish during the breeding in the culture facility. The scales or the skin of fish is usually discarded as an inedible tissue. Therefore, if the selenium level of such discarded tissues is about the same or higher compared with that of the ordinary muscle, in addition to no mercury accumulation, the new utilization of selenium will be expected as an essential element (not only detoxification of mercury) from the inedible tissues of marine products, including the improvement of environment.

In the present paper, the selenium distribution in the scales or skin as one of the inedible tissues of several species of cultured and wild fish was investigated in order to clarify the possibility of the utilization of selenium from those discarded tissues, in relation with the mercury distribution involving tissue.

2. Materials and methods

2.1 Materials

In cultured species, three, ten and five individuals of Yellow tail *Seriora quinqueradiata*, Red sea bream *Pagrus major* from

Oita Prefecture and Puffer *Takihugu rubripes* from Yamaguchi Prefecture were used in this study, respectively. On the other hand, in all wild species, three, nine and five individuals of Yellow tail, Red sea bream and Puffer from Fukuoka Prefecture were also used in this study, respectively. There was little deference of the degree of growth between wild and cultured species in each sampled fish.

In the present study, the ordinary muscle as edible tissue and the scales (skin only in the case of Puffer) as inedible tissue were removed from these fish bodies, and stored in a freezer until analyzed, and then submitted for analysis.

2.2 Methods

2.2.1 Determination of mercury

The total mercury concentration in each specimen was measured by a flow injection analysis system using cold vapor atomic absorption spectrometry (FIAS-CV-AAS) preceded by a wet digestion in a microwave oven, and abbreviated as T-Hg (Aduna de Paz et al., 1997).

2.2.2 Determination of selenium

The oxidation number of selenium exists as -2, +4, and +6 in aquatic organisms. The minus divalent selenium exists as an organic form, and this form will be the selenide species assigned to the selenohydryl groups (–SeH or SeHg and SeCd) substituting for the sulfur of the thiol group or bonding to heavy metals such as Hg and Cd. The chemical forms of the plus tetravalent and hexavalent seleniums will be selenite and selenate species joined to two neighboring thiol groups in the protein, respectively (Gasiewicz and Smith, 1978; Cappon and Smith, 1981; Iwata et al., 1982).

The total selenium concentration and the concentration of the low oxidation states of selenium (selenide and selenite species) (abbreviated as T-Se and [Org.Se+Se (IV)], respectively) in each specimen were then measured using gas chromatography with an electron capture detector (Toei and Shimoishi, 1981). The concentration of the selenate species was estimated by the difference between T-Se and [Org.Se + Se (IV)], and abbreviated as Se (VI).

3. Results and discussion

3.1 Mercury distribution

3.1.1 Yellow tail

The range of T-Hg in the ordinary muscle and scales of cultured species were 0.07_4 to 0.08_4 and 0.00_3 to $0.00_5 \,\mu$ g/g ($0.08_0 \pm 0.00_4$ and $0.00_4 \pm 0.00_1 \,\mu$ g/g as each mean concentration), respectively. On the other hand, those of wild species were 0.14_2 to 0.18_6 and 0.00_7 to $0.01_1 \,\mu$ g/g ($0.16_1 \pm 0.01_8$ and $0.00_4 \pm 0.00_2 \,\mu$ g/g as each mean concentration), respectively. Each mean mercury level is shown in Figure 1.

As Figure 1 shows, the mercury level of the scales in both species was significantly lower than that of the ordinary muscle, and was nearly zero or below the detection limit.



Figure 1: Mercury levels in (A) cultured and (B) wild Yellowtail

3.1.2 Red sea bream

The range of T-Hg in the ordinary muscle and scales of cultured species were 0.06_4 to 0.08_7 and 0.00_1 to $0.00_4 \ \mu g/g$ ($0.07_2 \pm 0.00_6$ and $0.00_3 \pm 0.00_1 \ \mu g/g$ as each mean concentration), respectively. On the other hand, those of wild species were 0.05_9 to 0.17_3 and 0.00_1 to $0.00_5 \ \mu g/g$ ($0.09_7 \pm 0.02_7$ and $0.00_3 \pm 0.00_1 \ \mu g/g$ as each mean concentration), respectively. Each mean mercury level is shown in Figure 2.

As Figure 2 shows, the mercury level of the scales in both species was significantly lower than that of the ordinary muscle, and was nearly zero or bellow the detection limit as



Figure 2: Mercury levels in (A) cultured and (B) wild Red sea bream

the case of Yellow tail.

3.1.3 Puffer

The range of T-Hg in the ordinary muscle and scales of cultured species were 0.04₈ to 0.05₈ and 0.00₃ to 0.00₈ μ g/g (0.05₁ \pm 0.00₄ and 0.00₅ \pm 0.00₂ μ g/g as each mean concentration), respectively. On the other hand, those of wild species were 0.03₆ to 0.08₄ and 0.00₅ to 0.01₅ μ g/g (0.06₃ \pm 0.01₉ and 0.00₈ \pm 0.00₄ μ g/g as each mean concentration), respectively. Each mean mercury level is shown in Figure 3.

As Figure 3 shows, the mercury level of the skin in both species was significantly lower than that of the ordinary muscle as the cases of Yellow tail and Red sea bream but was somewhat high compared with that of scales.



Figure 3: Mercury levels in (A) cultured and (B) wild Puffer

3.2 Selenium distribution

3.2.1 Yellow tail

The ranges of [Org.Se + Se (IV)], Se (VI) and T-Se in the ordinary muscle of cultured species were 0.09_1 to 0.10_6 , 0.14_6 to 0.16_3 and 0.23_7 to 0.26_6 µg/g ($0.10_0 \pm 0.00_6$, $0.15_4 \pm 0.00_7$ and $0.25_4 \pm 0.01_2$ µg/g as each mean concentration), respectively. Those in the scales were 0.16_2 to 0.17_7 , 0.12_0 to 0.24_6 and 0.29_7 to 0.40_8 µg/g ($0.16_8 \pm 0.00_6$, $0.18_8 \pm 0.05_2$ and $0.35_6 \pm 0.04_6$ µg/g as each mean concentration), respectively.

On the other hand, those in the ordinary muscle of wild species were 0.16_7 to 0.20_2 , 0.17_6 to 0.25_3 and 0.34_3 to 0.44_1 µg/g ($0.18_6 \pm 0.01_4$, $0.21_3 \pm 0.03_1$ and $0.39_9 \pm 0.04_1$ µg/g as each mean concentration), respectively. Those in the scales were 0.17_5 to 0.19_5 , 0.16_0 to 0.17_0 and 0.34_5 to 0.35_5 µg/g ($0.18_6 \pm 0.00_8$, $0.16_4 \pm 0.00_4$ and $0.35_0 \pm 0.00_4$ µg/g as each mean concentration), respectively. Each mean selenium level is shown in Figure 4.

As Figure 4 shows, the selenium level of the scales in both species was about the same as that of the ordinary muscle, not as in the case of the mercury level.



Figure 4: Selenium levels in (A) cultured and (B) wild Yellowtail

3.2.2 Red sea bream

The ranges of [Org.Se + Se (IV)], Se (VI) and T-Se in the ordinary muscle of cultured species were 0.04₃ to 0.06₄, 0.09₅ to 0.25₈ and 0.15₀ to 0.31₂ µg/g (0.05₆ \pm 0.00₇, 0.14₅ \pm 0.04₈ and 0.20₁ \pm 0.04₉ µg/g as each mean concentration), respectively. Those in the scales were 0.06₁ to 0.17₇, 0.07₆ to 0.39₈ and 0.22₂ to 0.51₀ µg/g (0.12₅ \pm 0.04₁, 0.23₀ \pm 0.09₆ and 0.35₅ \pm 0.10₉ µg/g as each mean concentration), respectively.

On the other hand, those in the ordinary muscle of wild species were 0.48_5 to 0.10_4 , 0.12_2 to 0.33_1 and 0.28_3 to 0.76_9 µg/g ($0.19_4 \pm 0.09_3$, $0.20_6 \pm 0.06_2$ and $0.40_0 \pm 0.12_8$ µg/g as each mean concentration), respectively. Those in the scales



Figure 5: Selenium levels in (A) cultured and (B) wild Red sea bream

were 0.12₃ to 0.35₅, 0.18₇ to 0.58₁ and 0.35₇ to 0.78₆ µg/g (0.19₄ \pm 0.05₄, 0.32₈ \pm 0.12₃ and 0.52₂ \pm 0.08₉ µg/g as each mean concentration), respectively. Each mean selenium level is shown in Figure 5.

As Figure 5 shows, the selenium level of the scales in both species was somewhat high compared with that of the ordinary muscle.

3.2.3 Puffer

The ranges of [Org.Se + Se (IV)], Se (VI) and T-Se in the ordinary muscle of cultured species were 0.09_2 to 0.28_2 , 0.02_5 to 0.18_8 and 0.21_7 to $0.30_5 \ \mu g/g$ ($0.14_0 \pm 0.07_2$, $0.12_5 \pm 0.05_5$ and $0.26_2 \pm 0.03_4 \ \mu g/g$ as each mean concentration), respectively. Those in the skin were 0.13_1 to 0.24_4 , 0.16_8 to 0.43_4 and 0.30_0



Figure 6: Selenium levels in (A) cultured and (B) wild Puffer

to $0.56_5~\mu g/g~(0.16_0\pm0.04_2,~0.25_0\pm0.09_7$ and $0.41_0\pm0.10_3~\mu g/g$ as each mean concentration), respectively.

On the other hand, those in the ordinary muscle of wild species were 0.06_9 to 0.10_0 , 0.09_9 to 0.22_9 and 0.18_3 to 0.30_6 μ g/g ($0.08_1 \pm 0.01_0$, $0.14_4 \pm 0.04_5$ and $0.22_6 \pm 0.04_2$ μ g/g as each mean concentration), respectively. Those in the skin were 0.10_2 to 0.20_4 , 0.10_2 to 0.25_3 and 0.27_4 to 0.35_5 μ g/g ($0.13_1 \pm 0.03_9$, $0.18_0 \pm 0.05_6$ and $0.31_1 \pm 0.02_8$ μ g/g as each mean concentration), respectively. Each mean selenium level is shown in Figure 6.

As Figure 6 shows, the selenium level of the scales in both species was somewhat high compared with that of the ordinary muscle as the case of Red sea bream.

4. Conclusion

Se/Hg (the molar ratio of selenium to mercury) of the ordinary muscle and the scales or the skin in all sampled fish species were estimated at molar basis as the indicator on the safety of marine products, from the point of the toxicological view of a trace amount of heavy metals such as mercury.

The ranges of Se/Hg in the ordinary muscle and the scales or the skin of cultured species were 2.89 to 15.81 and 140.99 to 1285.44, respectively. On the other hand, those of wild species were 5.10 to 21.95 and 6.45 to 1191.45, respectively. From the facts, the distribution profiles of both ratios were about the same, and those mean values were larger than 1, suggesting that those sampled marine products are generally safe against the toxicity due to the accumulation of mercury. Especially, it is very noteworthy that those values in the inedible tissues such as scales or skin were extremely high compared with those in the ordinary muscle. These findings mean that the new utilization of selenium as an essential element will be expected using the discarded tissues containing the present inedible tissues, and moreover that the improvement of environment will be performed by such utilization.

In further studies, using another species of fish, and shell crustaceans or seaweeds etc., the possibility of the overall utilization of selenium from discarded or inedible tissues in the marine products should be clarified.

References

- Aduna de Paz, L., Alegria, A., Barbera, R., Farre, R. and Lagarda, M. J. (1997). Detrmination of mercury in dry-fish samples by microwave digestion and flow injection analysis system cold vapor atomic absorption spectrometry. *Food Chemistry*, Vol.58, Nos.1&2, 169-172.
- Cappon, C. J. and Smith, J. C. (1981). Mercury and selenium content and chemical form in fish muscle. *Archives of Environmental Contamination and Toxicology*, Vol. 10, 305-309.
- Gasiewicz, T. A. and Smith, J. C. (1978). Properties of the cadmium and selenium complex formed in vivo and in vitro. *Chemico-Biological Interactios*, Vol. 23, 171-178.

- Iwata, H., Matsunaga, T., Kito, H. and Hayashi, M. (1982). Dedradation of methyl mercury by selenium. *Life Science*, Vol. 31, 859-866.
- Kai, N., Takahashi, Y., Kondo, M., Takeshita, N., Inoue, S., Tanoue, Y. and Nagai, T. (2007). The behavior of selenium and mercury in cultured fish-I: The profile of selenium distribution in cultured olive flounder. *ITE Letters*, Vol. 8, No.5, 106-109.
- Kai, N., Takahashi, Y., Kondo, M., Takeshita, N., Inoue, S., Tanoue, Y. and Nagai, T. (2008). The behavior of selenium and mercury in cultured fish-II: The profile of mercury distribution in cultured olive flounder. *ITE Letters*, Vol. 1, No. 5, 431-435.
- Kai, N., Takahashi, Y., Kondo, M., Takeshita, N., Inoue, S., Tanoue, Y. and Nagai, T. (2009). The behavior of selenium and mercury in cultured fish-III: The profile of selenium and mercury distribution In cultured olive flounder using extruder pellet. *ITE-IBA Letters*, Vol. 2, Nos. 5&6, 38-44.
- Kai, N., Takahashi, Y., Kondo, M., Takeshita, N., Inoue, S., Tanoue, Y. and Nagai, T. (2010). The behavior of selenium and mercury in cultured fish-IV: The profile of mercury distribution in red sea bream. *ITE-IBA Letters*, Vol. 3, No. 4, 31-35.
- Kai, N., Takahashi, Y., Kondo, M., Takeshita, N., Inoue, S., Tanoue, Y. and Nagai, T. (2011). The behavior of selenium and mercury in cultured fish-V: The profile of selenium distribution in red sea bream. *ITE-IBA Letters*, Vol. 4, No. 2, 15-20.
- Kai, N., Takahashi, Y., Kondo, M., Takeshita, N., Inoue, S., Tanoue, Y. and Nagai, T. (2011). The behavior of selenium and mercury in cultured fish-VI: The profile of mercury distribution in cultured amberjack. *ITE-IBA Letters*, Vol. 4, No. 2, 21-24.
- Kai, N., Takahashi, Y., Kondo, M., Tanoue, Y., Tanaka, R., Fukushima, H., Maeda, T., Fukuda, Y. and Nagai, T. (2012). The behavior of selenium and mercury in cultured fish-VII: The influence of the fasting upon the mercury and selenium distribution. *Studies in Science and Technology*, Vol. 1, No. 2, 103-105.
- Toei, K. and Shimoishi, Y. (1981). Detemination of ultra-micro amounts of selenium by gas chromatography with electron-capture detection. *Talanta*, Vol. 28, 967-972.

(Received: November 5, 2013; Accepted: November 19, 2013)