Original Article

The available utilization of selenium from some inedible tissues of marine products-V:
The distribution of selenium in several species of fish as the special marine products from Oita Prefecture

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Abstract
The selenium distribution in the scale, the skin or the endothelium as inedible tissues and the ordinary muscle of several species of fish (Japanese horse mackerel *Trachurus japonicus*, Chub mackerel *Scomber japonicus*, Largehead hairtail *Trichiurus lepturus* and Doggertooth pike conger *Muraenesox cinereus*) which have generally been known as the special marine products from Oita Prefecture was investigated in order to clarify the possibility of the available utilization of selenium especially from inedible tissues, in relation with the mercury distribution involving the tissues. As results, both levels of selenium and mercury in the ordinary muscle of the subjected fish were higher than those from the other ocean areas. Each mercury and selenium level in those inedible tissues of all subjected species was about the same and high compared with that involving muscle, respectively. On the other hand, from the selenium molar fraction involving inedible tissues, the low oxidation states of selenium species was almost predominant in all subjected species, as not in the case of involving ordinary muscle. The Se/Hg (the molar ratio of selenium to mercury) as an indicator of the safety of marine products was also extremely high compared with that involving ordinary muscle, suggesting that the scale, the skin or the endothelium will be usually inedible but significantly safe tissue in which little levels of heavy metals such as mercury will tend to accumulate, as in the case of a preceding paper. These findings suggested that the available utilization of selenium will be expected from the scale, the skin or the endothelium as inedible tissues of fish regardless of inhabiting waters, including the improvement of the environment.

Key words
selenium, mercury, distribution, special marine products, endothelium

1. Introduction

The inedible tissues of marine organisms are usually discarded. Therefore, if the selenium level of such discarded tissues is about the same or higher compared with that of the ordinary muscle as an edible tissue, in addition to little mercury accumulation, the available 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 the environment. We have already reported the selenium distribution in the inedible tissues of several species of marine organisms in relation with the mercury distribution involving tissue (Kai et al., 2013; 2014; 2017; 2018). As a result, each selenium level in the scales or skin and pectoral fin of fish was about the same or somewhat higher than that involving muscle of those fish, but the mercury level was surprisingly low or nearly zero, as not in the cases of midgut grand of shellfish (Kai et al., 2017).

Japanese horse mackerel and Chub mackerel from Saganoseki at Oita Prefecture has been well known as ”Seki Aji” and ”Seki Saba”, respectively. Moreover, in recent years, Largehead hairtail called as “Kunisaki Gintachi” and Doggertooth pike conger at the higher but a little-known producer in Japan have been commercialized as one of further branded marine foods, for purpose of the town revitalization in Oita Prefecture. It is well known that especially ”Seki Aji” and ”Seki Saba” stay fresh a long time and contain a large amount of umami components (Shigemura et al., 2004). However, there is little information on those special marine products from Oita Prefecture.

Therefore, in the present paper, we clarified first the selenium distribution in those special marine products, in relation with the mercury distribution involving the tissues. Moreover, the possibility of the available utilization of selenium from those inedible tissues was also discussed.

2. Materials and methods

2.1 Materials

Four kinds of fish (Japanese horse mackerel *Trachurus japonicus* called as ”Seki Aji”, Chub mackerel *Scomber japonicus* called as ”Seki Saba”, Largehead hairtail *Trichiurus lepturus* and Doggertooth pike conger *Muraenesox cinereus*). Both of Japanese horse mackerel and Chub mackerel were caught at Saganoseki. Largehead hairtail and Doggertooth pike conger was caught at Kunisaki and Kitsuki, respectively. Five individual ranges of body length of Japanese horse mackerel, Chub mackerel, Largehead hairtail and Doggertooth pike conger were 29.3 to 37.5, 25.8 to 29.8, 89.0 to 90.0 and 83.0 to 92.5 cm, respectively. There was little difference of the degree of growth between the same species in each sampled fish.

In the present study, the ordinary muscle as edible tissues and the scale, the skin or the endothelium as inedible tissues were removed from these fish bodies, and stored in a freezer at −30 °C until analyzed.

2.2 Methods

2.2.1 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 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 fluorometry (Toei and Shimoishi, et al., 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).

2.2.2 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).

3. Results and discussion

3.1 Selenium distribution

3.1.1 Japanese horse mackerel

The ranges of [Org.Se+Se(IV)], Se(VI) and T-Se in the ordinary muscle were 0.39_5 to 0.62_6, 0.036_3 to 0.88_3 μg/g and 0.80_9 to 1.42_8 μg/g (0.48_4±0.08_9, 0.55_2±0.19_3 and 1.03_6±0.22_5 μg/g as each mean concentration), respectively. Those in the scale were 0.41_1 to 0.87_6, 0.21_7 to 0.83_9 and 0.81_1 to 1.26_4 μg/g (0.66_9±0.16_5, 0.45_5±0.23_6 and 1.12_4±0.23_6 μg/g as each mean concentration), respectively.

3.1.2 Chub mackerel

The ranges of [Org.Se+Se(IV)], Se(VI) and T-Se in the ordinary muscle were 0.30_0 to 0.71_1, 0.38_6 to 1.15_0 and 0.82_4 to 1.86_1 μg/g (0.47_1±0.14_0, 0.67_4±0.25_8 and 1.14_5±0.37_4 μg/g as each mean concentration), respectively. Those in the skin were 0.81_9 to 1.58_2, 0.42_8 to 1.08_3 and 1.34_4 to 2.39_0 μg/g (1.08_5±0.26_2, 0.75_3±0.24_4 and 1.83_7±0.37_8 μg/g as each mean concentration), respectively.

3.1.3 Largehead hairtail

The ranges of [Org.Se+Se(IV)], Se(VI) and T-Se in the ordinary muscle were 0.24_0 to 0.39_9, 0.26_8 to 0.80_1 and 1.04_8 to 0.58_8 μg/g (0.28_6±0.06_0, 0.45_9±0.18_3 and 0.74_5±0.15_9 μg/g as each mean concentration), respectively. Those in the endothelium were 0.44_7 to 0.97_0 μg/g, 0.15_4 to 0.48_3 and 0.73_6 to 1.18_1 μg/g (0.66_2±0.19_1, 0.34_7±011_5 and 1.00_9±0.15_7 μg/g as each mean concentration), respectively.

3.1.4 Doggertooth pike conger

The ranges of [Org.Se+Se(IV)], Se(VI) and T-Se in the ordi-

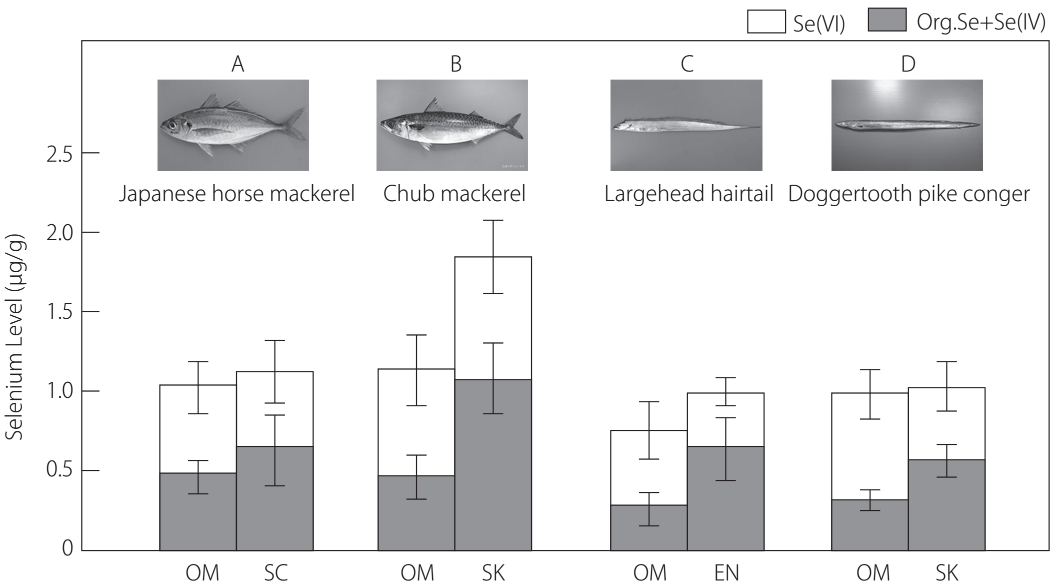

Figure 1: Selenium levels in the subjected fish

Notes: OM; Ordinary Muscle, SK; Skin, EN; Endothelium nary muscle were 0.12_9 to 0.40_6, 0.50_4 to 0.86_0 and 0.66_8 to 1.21_8 μg/g ($0.32_1 \pm 0.09_9$, $0.66_5 \pm 0.14_5$ and $0.98_6 \pm 0.20_3$ μg/gas each mean concentration), respectively. Those in the skin were 0.40_5 to 0.73_0, 0.27_0 to 0.68_6 and 0.78_3 to 1.41_8 μg/g ($0.57_1 \pm 0.11_8$, $0.45_9 \pm 0.14_2$ and $1.03_0 \pm 0.23_6$ μg/g as each mean concentration), respectively.

3.2 Mercury distribution

3.2.1 Japanese horse mackerel

The ranges of T-Hg in the ordinary muscle and scale were 0.02_9 to 0.06_5 and 0.00_3 to 0.00_8 μg/g ($0.04_8 \pm 0.01_2$ and $0.006 \pm 0.00_2$ μg/g as each mean concentration), respectively.

3.2.2 Chub mackerel

The range of T-Hg in the ordinary muscle and skin were $0.01_3$to 0.07_2 and 0.00_9 to 0.01_4 μg/g ($0.03_1 \pm 0.02_1$ and $0.01_7 \pm 0.01_1$ μg/g as mean concentration), respectively.

3.2.3 Largehead hairtail

The ranges of T-Hg in the ordinary muscle and endothelium were 0.03_7 to 0.07_6 and $0.01_8$to 0.05_5 μg/g ($0.05_6 \pm 0.01_4$ and $0.03_3 \pm 0.01_3$ μg/g as each mean concentration), respectively.

3.2.4 Doggertooth pike conger

The ranges of T-Hg in the ordinary muscle and skin were 0.06_5 to 0.25_0 and $0.02_8$to 0.05_6 μg/g ($0.13_9 \pm 0.06_6$ and $0.04_0 \pm 0.01_0$ μg/g as each mean concentration), respectively.

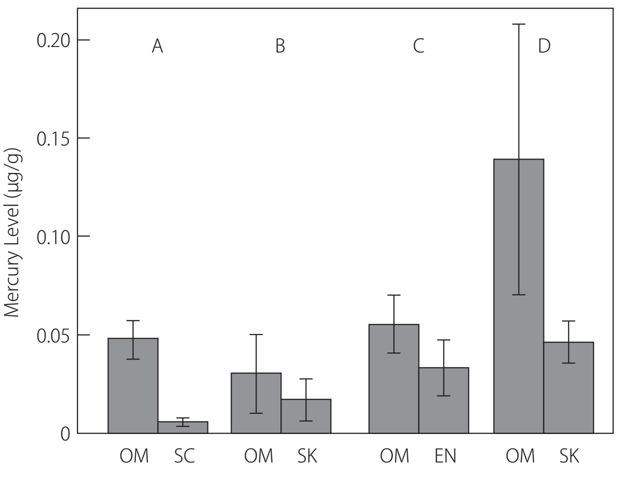

Figure 2: Mercury levels in the subjected fish

Notes: OM; Ordinary Muscle, SK; Skin, EN; Endothelium. A, B, C, and D refers to each subjected fish in Figure 1, respectively.

4. Conclusion

Both levels of selenium and mercury in the ordinary muscle of the subjected fish from Bungo Channel were higher than those from the other ocean areas (Kai et al., 2013 & 2014). Furthermore, from the estimated value of selenium molar fraction, the molar fraction of Se(VI) of ordinary muscle is about the same or higher than that or the discarded tissues, while the molar fraction of [Org.Se+Se(IV)] of the discarded tissues was about the same or somewhat higher than that of ordinary muscle in the subjected fish. However, it has been still now reported that the low oxidation states of selenium exist predominantly in the ordinary muscle of wild ocean fish (Cappon and Smith, 1981). Then, it is very noteworthy that those present results were different with those of previous reports. These findings may show the characteristics of marine ecosystem in present sea area, as in the case of the investigation by Shigemura et al, (Shigemura et al., 2004).

On the other hand, from the profiles of selenium and mercury distribution shown in Figures 1 and 2, it was clear that those of present fish are about the same, as in the cases of papers previously reported (Kai et al., 2013; 2014; 2017), that is, that the selenium levels of the discarded tissues (scale, skin or endothelium) are about the same or some what higher than those of the ordinary muscle, in addition to lower mercury accumulation. These findings may suggest the characteristics of marine ecosystem living in the present sea area, that is, there is a little mercury species as HgSe in the fish body by a prompt excretion of the detoxified compound as HgSe.

In the present fish, each molar ratio (Se/Hg) of T-Hg to T-Se in both tissues was also calculated as an indicator of safety against toxicity due to the accumulation of mercury (Storelli and Marcotrigiano, 2002; Kehrig et al., 2009; Kai et al., 2013; 2014; 2017; 2018). As the results, the ranges of Se/Hg of the ordinary muscle and scale in Japanese horse mackerel were 41.7_8 to 92.4_2 and $342.3_2$to 1058.5_0 ($54.8_3 \pm 18.7_9$ and $475.9_0 \pm 253.3_2$ as each mean value), respectively. Those of the molar ratio of the ordinary muscle and skin in Chub mackerel were 38.2_8 to 214.7_8 and 100.6_8 to 674.6_2 ($93.8_3 \pm 66.1_0$

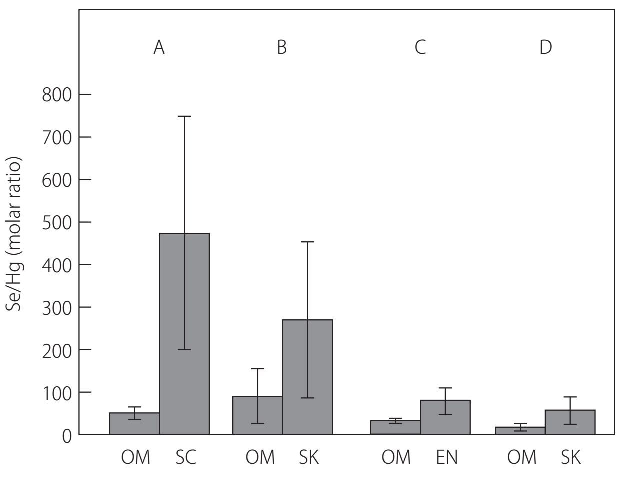

Figure 3: Se/Hg (molar ratio) in the subjected fish

Notes: OM; Ordinary Muscle, SK; Skin, EN; Endothelium. A, B, C, and D refers to each subjected fish in Figure 1, respectively.

and $274.5_1 \pm 181.6_2$ as each mean value), respectively. Those of the molar ratio of the ordinary muscle and endothelium in Largehead hairtail were 27.3_3 to 41.4_9 and 54.5_5 to 116.7_5 ($34.6_9 \pm 5.7_0$ and $85.8_7 \pm 22.2_6$ as each mean value), respectively. Those of the molar ratio of the ordinary muscle and skin in Doggertooth pike conger were 8.9_8 to 31.7_7 and 34.3_0 to 94.8_0 ($21.1_5 \pm 7.6_1$and $58.1_4 \pm 22.1_7$ as each mean value), respectively.

As shown in Figure 3, all of those mean values were larger than 1.00, suggesting that those sampled marine products are generally safe against toxicity due to the accumulation of mercury. These findings mean that the new utilization of selenium as an essential element will be expected using the especially inedible tissues of subjected fish

In further studies, using another species of crustaceans or seaweeds etc., the possibility of the overall utilization of selenium from the discarded or inedible tissues in marine products should be clarified. Furthermore, the characteristics of marine ecosystem in present sea area will also be clear.

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