Original Article

The available utilization of selenium from some inedible tissues of marine products-III:
The distribution of selenium in several species of shellfish

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Abstract
Each selenium distribution in the midgut gland, as one of the inedible tissues and whole muscle of the several species of bivalves and snails, was investigated in order to clarify the possibility of the available utilization of selenium from the inedible tissues of shellfish, in relation with mercury distribution involved in those tissues. Both levels in the midgut gland in all subjected shellfish was significantly high as that involving the whole muscle and low oxidation states of selenium species existed dominantly in both tissues. On the other hand, the Se/Hg (the molar ratio of selenium to mercury) in the midgut gland of those shellfish as an indicator of the safety of marine products was about the same or higher compared with that involving whole muscle, suggesting that the midgut gland is usually inedible but a significantly safe tissue. However, because the heavy metals such as mercury will tend to accumulate higher in the midgut gland compared with the whole muscle, as a result, the decrease of the molar fraction of bioavailable species of Se(VI) was observed in the midgut gland. These findings suggested that the available utilization of selenium will not be expected from the midgut gland of shellfish, as was not the case of several species of fish previously reported.

Key words
selenium, mercury, distribution, midgut gland, shellfish

1. Introduction

If the selenium level in inedible tissues of fish and shellfish is about the same or higher compared with that of 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 environment.

Therefore, it has already been reported that the selenium distribution in the scales or skin as the inedible tissues of several species of fish in relation with the mercury distribution involving tissue (Kai et al., 2013; 2014). As a result, each selenium level in the scales or skin was about the same or somewhat higher than that involving muscle of those fish, however the mercury level was surprisingly low or nearly zero.

In recent years, it has been well known that the midgut gland is one of the tissues in relation to the shellfish poison and so not usually ingested and discarded to avoid a risk (Asakawa et al., 1986; Takata et al., 2004). Then, it is noteworthy to investigate if the selenium level of such discarded tissues in shellfish is about the same or higher compared with that of the ordinary muscle, in addition to lower or little mercury accumulation, because the available utilization of selenium may be newly found from the inedible tissues such as the scales or the skin of fish.

In this present paper, the selenium distribution in the midgut gland was investigated as one of inedible tissues of the several species of shellfish in order to clarify the possibility of the utilization of selenium from those tissues, in relation with the mercury distribution involved in the tissue.

2. Materials and methods

2.1 Materials

Five individuals of bivalves and snails were submitted in this present study.

2.1.1 Bivalves

The ranges of shell length of Pen shell *Atrina pectinata* from Saga Prefecture and Scallops *Patinopecton yessoensis* were 9.1 to 11.0 and 12.8 to 14.1 cm, respectively.

2.1.2 Snails

Five individuals of herbivorous and carnivorous species were submitted in this present study.

2.1.2.1 Herbivorous species

The ranges of shell length of Turban shell *Turbo comtus* and Matsubagai *Cellana nigrolineata* from Yamaguchi Prefecture were 6.0 to 7.0 and 4.0 to 5.0 cm, respectively.

2.1.2.2 Carnivorous species

The ranges of shell length of Whelk *Babylonia japonica* from Kagoshima Prefecture and Veined rapa whelk *Rapana venosa* from Fukuoka Prefecture were 4.5 to 5.0 and 10.0 to 10.2 cm, respectively.

There was little defference of the degree of growth between the same species in each shellfish described above.

In the present study, the whole muscle and the midgut gland as inedible tissues were removed from these shellfish 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 is the selenide species assigned to the selenohydryl groups (–SeH or SeHg and SeCd) substituting for sulfur of the thiol group or the bonding to heavy metals such as Hg and Cd. The chemical forms of the plus tetravalent and hexavalent seleniums are 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 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).

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 Bivalves

3.1.1.1 Pen shell

The ranges of [Org.Se+Se(IV)], Se(VI) and T-Se in the whole muscle were 0.09_8 to 0.25_9, 0.01_3 to 0.16_2 and 0.17_4 to 0.33_0 μg/g ($0.15_1 \pm 0.04_4$, $0.08_0 \pm 0.04_4$ and $0.23_2 \pm 0.05_2$ μg/g as each mean concentration), respectively. Those in the midgut gland were 0.53_4 to 0.99_0, 0.02_1 to 0.29_7 and 0.60_0 to 1.17_0 μg/g ($0.73_9 \pm 0.15_6$, $0.14_9 \pm 0.08_8$ and $0.88_8 \pm 0.19_6$ μg/g as each mean concentration), respectively.

3.1.1.2 Scallops

The ranges of [Org.Se+Se(IV)], Se(VI) and T-Se in the whole muscle were 0.07_3 to 0.12_7, 0.02_7 to 0.34_1 and 0.11_4 to 0.43_5 μg/g ($0.09_9 \pm 0.01_9$, $0.11_8 \pm 0.09_5$ and $0.21_7 \pm 0.10_0$ μg/g as each mean concentration), respectively. Those in the midgut gland were 0.59_6 to 0.91_3, 0.02_8 to 0.32_1 and 0.66_4 to 1.04_3 μg/g ($0.70_2 \pm 0.11_2$, $0.14_3 \pm 0.09_1$ and $0.84_5 \pm 0.19_6$ μg/g as each mean concentration), respectively.

3.1.2 Snails

3.1.2.1 Herbivorous species

3.1.2.1.1 Turban shell

The ranges of [Org.Se+Se(IV)], Se(VI) and T-Se in the whole muscle were 0.10_9 to 0.16_7, 0.01_7 to 0.07_6 and 0.16_4 to 0.18_7 μg/g ($0.14_1 \pm 0.01_0$, $0.04_0 \pm 0.01_0$ and $0.18_1 \pm 0.00_4$ μg/g as each mean concentration), respectively. Those in the midgut gland were 0.43_3 to 0.75_1, 0.02_0 to 0.33_4 and 0.46_1 to 0.98_0 μg/g ($0.57_4 \pm 0.05_8$, $0.10_4 \pm 0.05_9$ and $0.67_8 \pm 0.10_1$ μg/g as each mean concentration), respectively.

3.1.2.1.2 Matsubagai

The ranges of [Org.Se+Se(IV)], Se(VI) and T-Se in the whole muscle were 0.09_7 to 0.12_3, 0.01_6 to 0.04_3 and 0.11_6 to 0.16_3 μg/g ($0.10_4 \pm 0.00_0$, $0.03_2 \pm 0.00_5$ and $0.13_6 \pm 0.00_8$ μg/g as each mean concentration), respectively. Those in the midgut gland were 0.14_0 to 0.37_5, 0.00_6 to 0.06_9 and 0.15_6 to 0.39_0 μg/g ($0.23_7 \pm 0.04_6$, $0.04_1 \pm 0.01_3$ and $0.27_8 \pm 0.04_6$ μg/g as each mean concentration), respectively.

3.1.2.2 Carnivorous species

3.1.2.2.1 Whelk

The ranges of [Org.Se+Se(IV)], Se(VI) and T-Se in the whole muscle of cultured species were 0.21_2 to 0.30_0, 0.08_7 to 0.51_0 and 0.34_6 to 0.78_8 μg/g ($0.25_8 \pm 0.01_5$, $0.22_6 \pm 0.07_5$ and $0.48_4 \pm 0.07_9$ μg/g as each mean concentration), respectively. Those in the midgut gland were 0.67_6 to 1.38_9, 0.10_4 to 1.08_3 and 0.87_7 to 2.17_5 μg/g ($1.06_5 \pm 0.14_6$, $0.48_6 \pm 0.18_6$ and $1.55_1 \pm 0.28_3$ μg/g as each mean concentrat ion), respectively.

3.1.2.2.2 Veined rapa whelk

The ranges of [Org.Se+Se(IV)], Se(VI) and T-Se in the whole muscle were 0.09_9 to 0.16_8, 0.00_5 to 0.10_1 and 0.14_1 to 0.24_6 μg/g ($0.12_8 \pm 0.01_3$, $0.06_6 \pm 0.01_6$ and $0.19_4 \pm 0.01_7$ μg/g as each mean concentration), respectively.

Those in the midgut gland were 0.74_2 to 0.90_6, 0.13_5 to 0.25_2 and 0.99_0 to 1.08_6 μg/g ($0.84_6 \pm 0.03_8$, $0.20_1 \pm 0.02_9$ and $1.04_7 \pm 0.01_9$ μg/g as each mean concentration), respectively.

The analytical data of selenium in all samples described above are shown in Figure1.

3.2 Mercury distribution

3.2.1 Bivalves

3.2.1.1 Pen shell

The range of T-Hg in the whole muscle and midgut gland were 0.00_1 to 0.01_0 and 0.01_0 to 0.02_2 μg/g ($0.00_4 \pm 0.00_2$ and $0.01_6 \pm 0.00_5$ μg/g as each mean concentration), respectively.

3.2.1.2 Scalops

The range of T-Hg in the whole muscle and midgut gland were 0.00_1 to 0.00_6 and 0.00_3 to 0.02_3 μg/g ($0.00_3 \pm 0.00_2$ and $0.01_3 \pm 0.00_6$ μg/g as each mean concentration), respectively.

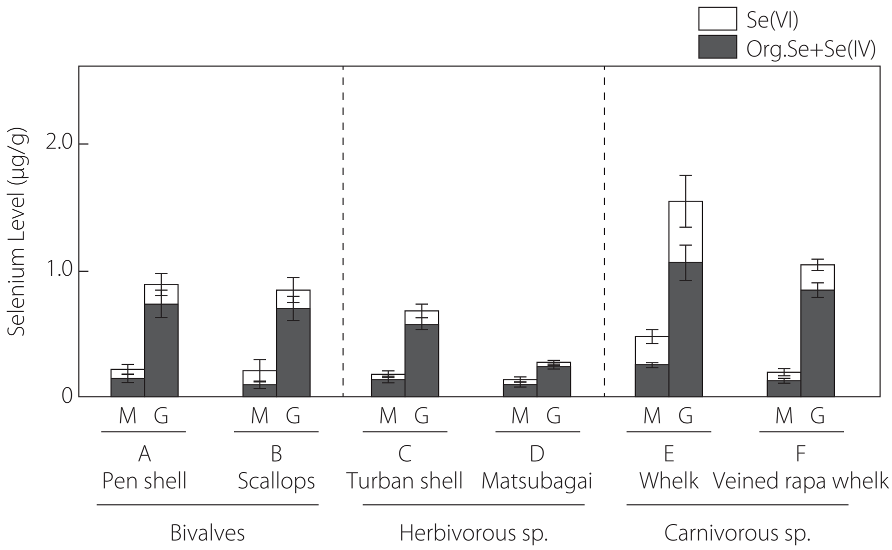

Figure 1: Selenium levels in the subjected shellfish

Note: M: Whole muscle; G: Midgut gland

3.2.2 Snails

3.2.2.1 Herbivorous species

3.2.2.1.1 Turban shell

The range of T-Hg in the whole muscle and midgut gland were 0.00_6 to 0.00_7 and 0.00_8 to 0.02_2 μg/g ($0.00_6 \pm 0.00_0$ and $0.01_3 \pm 0.00_2$ μg/g as each mean concentration), respectively.

3.2.2.1.2 Matsubagai

The range of T-Hg in the whole muscle and midgut gland were 0.00_6 to 0.02_1 and 0.00_7 to 0.03_8 μg/g ($0.01_4 \pm 0.00_3$ and $0.02_3 \pm 0.00_9$ μg/g as each mean concentration), respectively.

3.2.2.2 Carnivorous species

3.2.2.2.1 Whelk

The range of T-Hg in the whole muscle and midgut gland were 0.02_2 to 0.06_4 and 0.02_4 to 0.17_1 μg/g ($0.04_4 \pm 0.00_9$ and $0.12_4 \pm 0.02_7$ μg/g as each mean concentration), respectively.

3.2.2.2.2 Veined rapa whelk

The range of T-Hg in the whole muscle and midgut gland were 0.03_0 to 0.08_1 and 0.08_0 to 0.19_9 μg/g ($0.05_9 \pm 0.01_1$ and $0.15_5 \pm 0.02_6$ μg/g as each mean concentration), respectively.

The analytical data of mercury in all samples described above are shown in Figure 2.

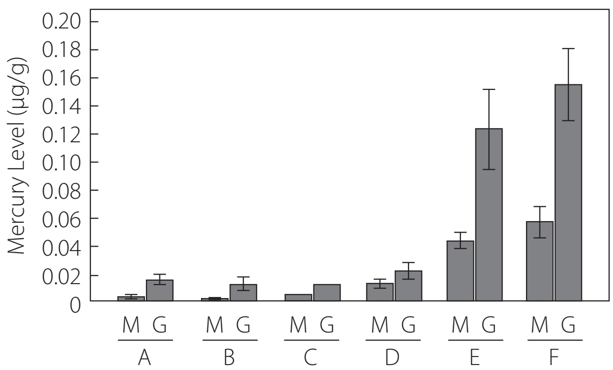

Figure 2: Mercury levels in the subjected shellfish

Notes: M: Whole muscle; G: Midgut gland. A, B, C, D and F refers to each subjected shellfish in Figure 1, respectively.

4. Conclusion

From the profiles of selenium and mercury distribution shown in Figures 1 and 2, it was clear that those of shellfish are significantly different to the cases of previous papers (Kai et al., 2013; 2014), that is, that the selenium levels of the midgut gland as discarded tissues are also high compared with those of the whole muscle, in addition to higher mercury accumulation. Furthermore, from the estimated value of selenium molar fraction shown in Figure 3, [Org.Se+Se(IV)]molar fraction of the midgut gland was about the same or somewhat higher than that of the whole muscle in the subjected shellfish, suggesting that some Se(VI) species as metabolized in a living body after eating, exists in the midgut glands. These findings mean that the new utilization of selenium as an essential element will be not expected using the midgut gland as inedible tissues of shellfish.

In the shellfish, each molar ratio 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 (Kai et al., 2013; 2014; 2016). The ranges of each mean molar ratio of the whole muscle and midgut gland were 8.35 to 259.39 and 17.16 to 233.11, respectively. The involved ratios are shown decreasing with the increase of trophic level on the food chain order at a marine ecosystem in Figure 4, and then all of those mean values were larger than 1, suggesting that those

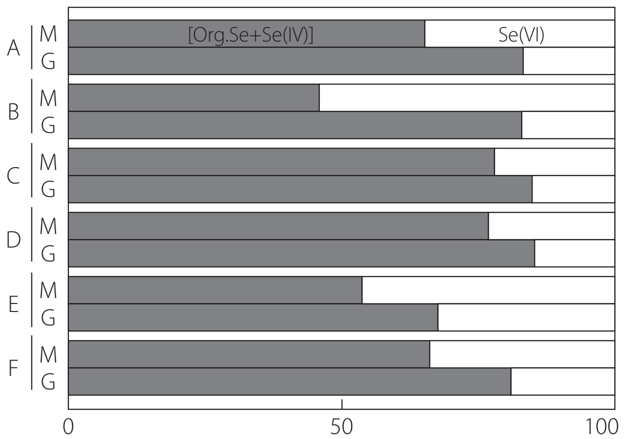

Figure 3: Selenium molar fraction in the subjected shellfish

Notes: M: Whole muscle; G: Midgut gland. A, B, C, D and F refers to each subjected shellfish in Figure 1, respectively.

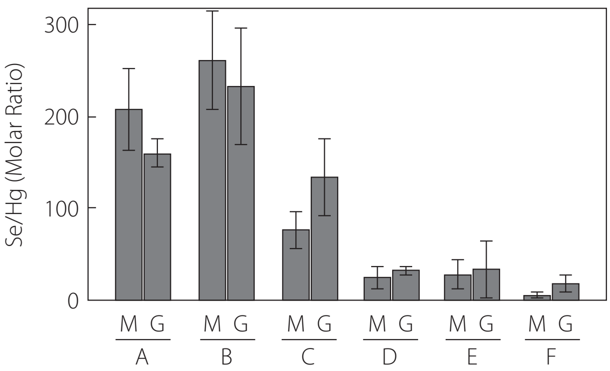

Figure 4: Se/Hg (molar ratio) in the subjected shellfish

Notes: M: Whole muscle; G: Midgut gland. A, B, C, D and F refers to each subjected shellfish in Figure 1, respectively.

sampled marine products are generally safe against toxicity due to the accumulation of mercury.

On the other hand, Figure 4 suggests that the higher the trophic level is, the lower the involved Se/Hg (molar ratio) is in a marine ecosystem, because those values of tuna or marine mammals are nearly 1 (Kai et al., 2000; Koeman, et al.,1973). Therefore, Se/Hg (molar ratio) may also be used as an indicator of the high and low order of trophic level on the food chain in relation to the increase of mercury accumulation with the trophic level on the food chain as in Figure 2.

In further studies, it is important to clarify, using crustaceans or seaweeds etc., the possibility of the overall utilization of selenium from the discarded or inedible tissues in marine products.

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