Health Benefit Value of Selenium (HBV-Se) of mercury from consumption of fishes from Tual, Indonesia

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Abstract. Our study reports the total mercury (THg) and total selenium (TSe) content measured in the tissue of fishes from the market at Tual (Indonesia), that was used to examine the Health Benefit Value of Selenium (HBV-Se) as a food safety index from mercury contamination in seafood consumption. Nine fish species that were usually eaten and predicted to have a high content of mercury were bought from the fish market. Direct Mercury Analyzer (DMA) NIC-MA3000 was used to analyze the total mercury (THg) content directly. While the fish sample for total selenium analysis must be prepared with microwave digestion prior to measure by ICP-OES. The mean THg concentrations varied from 0.009 up to 1.38 mg/kg-DW and the mean TSe concentrations varied from 1.56 up to 6.88 mg/kg-DW. Cephalopholis sonnerati and Epinephelus morrhaea exceeded the SNI standard which has a limit of 0.5 mg/kg, but all the fishes exceeded the new BPOM guidelines (0.06 mg/kg) except Siganus lineatus. The THg values from the highest were Epinephelus morrhaea > Cephalopholis sp > Cephalopholis ongus > Lutjanus gibbus > Epinephelus ongus > Euthynus affinis > Rastrelinger kanagurta > Katsuwanus pelamis > Siganus lineatus. Measurement of HBV-Se value of all the fishes in Tual showed positive values, which means safe for consumption. HBV-Se index provided a comprehensive elucidation of human risk assessment on food safety compared with the single data of total mercury due to mercury contamination.

1. Introduction

Fish is generally known as the main source of high-value protein and essential nutrient which makes fish is promoted as an important element of a healthy diet [1]. Furthermore, fish is also containing polyunsaturated fatty acid such as omega-3 that can be beneficial for reducing heart disease and promotes the proper growth and development in fetuses and children [2–4]. Mercury (Hg) can be found in the environment that originally come from natural and anthropogenic activities [5]. Several origins of natural processes releasing mercury including vegetation surfaces [6,7], water bodies [8,9], wild fires [10–12], as well as the re-emission of deposited mercury [13]. These processes are believed to release mainly Hg³ [13]. In nature, the inorganic forms of mercury (Hg³ and Hg (II)) are easily modified into organic form [8]. Methyl mercury, CH₃Hg⁺, and dimethyl mercury, (CH₃)₂Hg in water reservoirs can emerge to the environment, both as results of chemical reactions and under the impact of biological factors like microorganism [14,15]. Inorganic mercury is considerably less toxic than methyl mercury. Methyl mercury is highly toxic, mainly to the nervous system and also the developing brain as the most sensitive target organ. It is also considered the most important toxic compound in the aquatic food
web [16]. This chemical compound comes into the ocean food chain and achieves its highest concentration in the fish tissue as the top consumer/predator, and methyl mercury (MeHg) form is about 80% to 95% of the total mercury [17,18].

The newest guideline from Indonesian National Agency of Drug and Food Control (BPOM) No. 23/2017 has been applied, which states that none of the seafood product is worth to be consumed if the value of total Hg concentration exceeds the guideline (0.06 mg/kg). Up to now, mercury contamination on seafood product in Indonesia is still based on the total Hg content alone [19]. Health Benefit Value of Selenium (HBV-Se index) is a value of Se-Hg ratio developed as a result of Hg toxicity; which objective is to evaluate the relative effect of contamination of Hg with the presence of selenium (Se) in it. The HBV-Se index indicates the level of selenium content in fish tissue contrasted to CH₃Hg concentration, which offers a more credible index for evaluating mercury contamination risk [20]. Fisheries commodities that have negative index values are suggested not to be eaten. The negative value on the index represents the level of mercury content that is higher than the Selenium content [20]. The aim of this research was to examine the presence of mercury in the fish consumed in Tual, Southeast Maluku, Indonesia and comparing the total mercury (THg) with three seafood safety guideline standards i.e. Indonesian National Standard (SNI No. 7387-2009), Joint FAO/WHO Food Standards (JECFA) and BPOM Guidelines No. 23/2017.

2. Methodology

2.1. Samples
This study was conducted in April–June 2018. All the samples were bought from local markets in Tual, Southeast Maluku, Indonesia and directly frozen. The fish fillet of big fish was the only part that was used for analysis, while for small and medium-sized fish the whole of body part was used except the head, skin and tail for the medium-sized fish. Before the fish sample was prepared for mercury and selenium analysis, morphometric analysis was done by measuring the length and weight of fish. Then, fish tissues were filleted, homogenised, dried (40°C, 48 h), and ground into a fine powder then stored in zip lock plastic bag.

2.2. Reagent and instrumentation
All reagents used were of analytical reagent grade (Merck) for Hg measurement unless otherwise stated. L-Cysteine was obtained from Nacalai Tesque Inc. (Japan). The solutions were prepared using ultrapure water (Milli-Q). The total mercury analysis was carried out by using Direct Mercury Analyzer (DMA) NIC MA 3000 while the total selenium was measured with a Thermo ICP OES iCAP 7400. An analytical balance (Sartorius BP210S), ruler and digital calliper were used for morphometric measurement. An oven (Heraeus Instrument), petri dish, spatula, scissors, mortar and pestle were used to prepare dried samples.

2.3. Total mercury and selenium analysis
The homogenised powdered sample 25 mg in three replicates was weighed with the sample boat directly and analyzed in DMA for total mercury concentration. Total selenium content measurement was performed in triplicates for each population by weighing 0.50 g of the powdered sample, added with 10 mL HNO₃ (65%) and heated up at 190°C for 30 minutes [21]. The digested powdered samples were diluted with Milli-Q water until 50 mL and stored in polyethylene bottles.

2.4. Data analysis
Total mercury content in the fish sample was contrasted to several standard guidelines [19,22,23]. The dry weight (DW) values of mercury and selenium were converted into wet weight (WW) by using a conversion of total moisture [24] for calculation of HBV-Se index using the following formula.

$$\text{HBV-Se} = \left[\frac{\text{Se-Hg}}{\text{Se}}\right] \times \left(\text{Se} + \text{Hg}\right)$$  [20]
3. Results and discussion

The result shows that the concentration of mercury was varied from 0.009 mg/kg-DW in Siganus lineatus to 1.38 mg/kg-DW in Epinephelus morrhua. All the THg values were under the SNI guidelines, for maximum concentration is 0.5 mg/kg for marine products, except for Cephalopholis sonnerati and Epinephelus morrhua. Table 1 exhibits the morphometric values and total mercury and selenium concentration (mean ± standard deviation) in fish sample stated as mg per kg of edible part (dry weight). The total mercury values from the highest were Epinephelus morrhua > Cephalopholis sonnerati > Cephalopholis miniata > Lutjanus gibbus > Epinephelus ongus > Euthynus affinis > Rastrelinger kanagurta > Katsuwonus pelamis > Siganus lineatus. When linked to the newest BPOM standard, all values surpassed the limit of the standard at 0.06 mg/kg except Siganus lineatus. Therefore, if the BPOM guidelines for seafood and marine products had been implemented, only Siganus lineatus was safe to be eaten. It is also indicated that carnivorous fishes always had higher mercury contents than omnivorous fish. Stergiou and Karpouzi [25] reported that the variation of fish food type depends on their living environment which could be demersal, benthopelagic, pelagic, bathy-demersal, and reef-associated with fish living and feeding on or near coral reefs.

Table 1. Morphometric, THg and TSe in fish samples from Tual.

| Scientific name (Local name) | N | Length (cm) | Weight (g) | Moisture content (%) | THg (mg/kg-DW) | TSe (mg/kg-DW) |
|------------------------------|---|-------------|------------|----------------------|----------------|---------------|
| Euthynus affinis (Tongkol)   | 8 | 33-44       | 436-873    | 73.15                | 0.269±0.13     | 2.59±1.07     |
| Rastrelinger kanagurta (Kembung) | 8 | 30-33.5     | 302-470    | 74.47                | 0.114±0.03     | 4.09±0.92     |
| Katsuwonus pelamis (Cakalang) | 5 | 39.5-42.5   | 1172       | 72.10                | 0.107±0.03     | 5.85±1.19     |
| Lutjanus gibbus (Jenaha)     | 7 | 23.5-30.3   | 192-434    | 80.7                 | 0.387±0.11     | 2.49±0.59     |
| Cephalopholis miniata (Kerapu) | 2 | 24.5-27.5   | 352-354    | 77.54                | 0.428±0.07     | 4.60±0.04     |
| Epinephelus ongus (Goropa)   | 3 | 28.5-46     | 310-498    | 79.50                | 0.345±0.05     | 1.56±0.89     |
| Cephalopholis sonnerati (Kerapu suu) | 1 | 29.9       | 461        | 77.32                | **0.946**      | 6.88          |
| Epinephelus morrhua (Kerapu besar) | 1 | 46         | 1445       | 79.19                | **1.383**      | 3.17          |
| Siganus literatus (Baronang)  | 5 | 25.5       | 291-459    | 76.43                | 0.009±0.004    | 2.19±0.32     |

* Values in bold indicate exceeding SNI and JECFA guidelines [22,23]

The concentration of total selenium (TSe) varied from 1.56 mg/kg in Epinephelus ongus to 6.88 mg/kg in Cephalopholis sonnerati. Since selenium is one of the essential elements, therefore, it is crucial to ensure the recommended selenium value in the fish on a daily basis based on the size and species of fish. Selenium is also one of the main agents for detoxifying mercury and methyl mercury [26]. Most fishes from Tual contained selenium at concentrations higher than Hg. Ralston et al. [27] declared that consuming fish from the low-Se area would pose greater risks to mercury contamination than eating Se-rich fish that contain the same amount of CH₃Hg.

Based on the result of HBV-Se index analysis shown in Figure 1, all the values show positive values, indicated that selenium content was higher than mercury content, therefore we believed that fishes collected from Tual’s water were safe and worth to be consumed. The HBV-Se equation indicates the level of selenium content in fish tissue contrasted to CH₃Hg concentration which offering a more credible index for evaluating mercury contamination risk [20]. Ralston et al. [27] stated that assessment...
of only methyl mercury or THg will give inaccurate measurement and interpretation on the effect of Hg toxicity, except if selenium is also taken into account in the evaluation.

Figure 1. The index of HBV-Se in fish tissues that originated from Tual.

4. Conclusion
Based on the measurement of HBV-Se, fishes from Tual are worth to be consumed even though some fishes already exceeded the permissible guideline limit from SNI 2009, JECFA 2006 and BPOM RI 2017. Measurement of THg as single data for human risk assessment will show different interpretation due to Hg toxicity. HBV-Se will give more information about human risk assessment of mercury consumption of marine fish. Limiting fish consumption based on body weight and age will minimize the effect on mercury bio-accumulation in the human body.

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