A preliminary study of metal accumulation in fish from Cimanuk and Cimandiri, West Java, Indonesia

R Puspitasari*, T Purbonegoro, S Oktaviyani, R Rositasari and M T Kaisupy

Research Centre for Oceanography, Indonesian Institute of Sciences, Jakarta, Indonesia

*Corresponding author e-mail: poespitsari@gmail.com

Abstract. Fish is known to be a source of animal protein consisting of low cholesterol and non fatty acid. It also promotes sustainable consumption in coastal communities. Metal contamination in aquatic bodies, particularly rivers and oceans, is made more likely by anthropogenic factors. Metal may accumulate in fish as a result of the food web, posing a health risk to humans. Metal contamination in ingested fish should be monitored as part of risk mitigation. The goal of this research was to investigate six elements (Cr, Cu, Se, Pb, Cd, and As) in the edible tissues of fish from Cimanuk and Cimandiri, West Java. Karangsong and Palabuhan Ratu were two locus of fishing ports in Cimanuk and Cimandiri, respectively. In April of 2017, commercial demersal fish were obtained. Three fish from Palabuhan Ratu and four fish from Karangsong were captured. Metal analysis was conducted using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP OES). The results revealed that the non-essential elements such as cadmium (Cd) and arsenic (As) had exceeded the permissible limits of the BPOM. Practically, organic arsenic (arsenobetain) is the most common arsenic found in fish (90-95%), and relatively safe compared to inorganic arsenic. Indications of Cd enrichment can come from anthropogenic factors and reinforce the necessity for environmental monitoring of habitats around fishing areas. Essential metals like selenium, copper, and chromium are maintained at a certain concentration based on metabolic activity and vary according to fish body homeostasis.

1. Introduction

West Java Province is one of the marine fishery sites in Indonesia that has direct access to the Indian Ocean in the south and the Java Sea in the north. Two main fish landing locus in this province are the Nusantara Fishery Port (PPN) Palabuhan Ratu, Cimandiri, Sukabumi and Fish Landing Base (PPI) Karangsong, Cimanuk, Indramayu. PPN Palabuhan Ratu supports the supply of fish to Jakarta, Bogor and surrounding areas. In general, Palabuhan Ratu fishermen catch fish in the Bay of Palabuhan Ratu and the Indian Ocean which is the Indonesian Republic's Fisheries Management Area (WPP-RI) 573. Meanwhile, for PPI Karangsong mostly carries out its fishing activities on the north coast of Indramayu and Java Sea or including WPP RI 712 [1].

Fish is a source of animal protein that is low in cholesterol, contains unsaturated fatty acids and essential nutrients that are good for health [2]. However, anthropogenic factors in aquatic ecosystems pose a risk of contamination in fish. Anthropogenic sources can be metal, organic, and other
contamination. Metal accumulation in fish can be sourced from their environment such as water and sediment, and move through the food chain [3]. The highest risk of accumulation occurs in the human being considered as the highest consumer in the food pyramid structure.

The essential elements (Cr, Cu and Se) are important for the enzymes-forming elements, redox reactions [2] and body metabolism [4]. The increase in non-essential metals from certain amounts can cause cell and tissue damage. Metals Pb, Cd and As are known to have no biological function so they are classified as non-essential elements and are toxic at low concentrations [4, 5, 6]. Monitoring of metal contamination is a mitigation for food safety both for domestic consumption and export reasons. The rejection of several fishery products from Indonesia to several countries such as the European Union and Korea in the period 2008-2017 was mostly caused by metal contamination factors, namely mercury, lead and arsenic, followed by microbiological factors [7]. The purpose of this study was to analyze the levels of six metals, namely Cr, Cu, Se, Pb, Cd, and As in commercial fish in the Cimanuk and Cimandiri areas, West Java.

2. Materials and Methods

2.1. Sampling

Fish samples were obtained from PPN Palabuhan Ratu, Cimandiri and PPI Karangsong, Cimanuk in April 2017. Three species from Palabuhan Ratu were Psettodes erumei (Sidefish), Epinephelus spilotoceps (grouper), Elagatis bipinnulata (Salem) while four species of fish from Karangsong. They are Abalistes stellatus (Etong fish), Leignathus equulus (Pepetek fish), Psettodes erumei (Sidefish), and Upeneus sulphureus (Kuniran fish) [8]. Fish were kept frozen prior to analysis.

![Figure 1](image-url) Sampling locations in Palabuhan Ratu, Cimandiri and Karangsong, Cimanuk.

The target fish are demersal fish, i.e. fish that live on or near the bottom of the water and are not fast swimmers, assuming that their home range is limited and not too wide. All fish were measured in length, weighed, identified to the species level, documented and sampled coded. The fish were rinsed with distilled water and dissected with a ceramic knife. The samples were dried in the Herraeus Oven for 24 hours at 60°C. The fish samples were then grinded manually into a homogenous powder using a mortar and pestle. Moisture content was measured by drying tissue in an oven at 105°C for 24 hours [9].

Sample preparation using a mixture of acids (9 ml 65% HNO₃, Merck and 3 ml 37% Merck HCl) was added to 0.5 grams of the sample. The mixture was then heated in a microwave oven CEM MARS 5 Express at 185°C for 15 minutes and allowed to stand for 30 minutes. The solution was filtered with Whatman paper no. 41. The filtrate was dissolved to 25ml with aquabides and measured at ICP OES 7400 Thermo [10].
2.2 Data Analysis
The metal content in dry weight is converted into wet weight by taking into account the water content factor [9]. Metal content in wet weight units is compared with metal contamination limits from BPOM and SNI. The metal contamination limit regulated by the National Agency of Drug and Food Control (2018) is 0.1 ppm for cadmium; 0.25 ppm for arsenic and 0.2 ppm for lead [11]. This limit is lower than the reference set by the National Standardization Agency (2019), which is 0.1 ppm for cadmium, 1 ppm for arsenic and 0.3 for lead [12]. Contamination standards set nationally only set limits for non-essential metals such as As, Pb and Cd, and do not regulate essential metals such as Se, Cu and Cr. This standard refers to international regulation, namely JECFA (The joint FAO/WHO Expert Committee on Food Additives).

3. Result and Discussion
The morphometry of samples of demersal fish consumed from Cimanuk and Cimandiri waters is shown in Table 1. The water content of fish samples ranged from 3.62 to 26.36%. The fish species in this study were the families Solenidae, Serranidae, Scrombidae, Balistidae, Leiognathidae, and Mullidae.

| Location       | Scientific Name       | Family                      | Length (cm) | Weight (g)  |
|----------------|-----------------------|-----------------------------|-------------|-------------|
| Palabuhan Ratu, Cimandiri | *Psettodes erumei*    | Soleidae                    | 27.5-29     | 312-354     |
|                | *Epinephelus spilotoceps* | Serranidae                 | 28.8-29.2   | 350-443     |
|                | *Elagatis bipinnulata* | Scrombidae                  | 28.6-29.5   | 226-285     |
| Karangsong, Cimanuk | *Abalistes stellatus*  | Balistidae                  | 32.5-32.6   | 626-721     |
|                | *Leiognathus equulus* | Leiognathidae               | 15.6-16.7   | 54-74       |
|                | *Psettodes erumei*    | Soleidae                    | 27.2-30.8   | 271-422     |
|                | *Upeneus sulphureus*  | Mullidae                    | 12.3-13.5   | 28-33       |

The highest metal content of As and Cd was found in Etong fish, the highest Se metal content in Kuniran fish and the highest Cu content in Salem fish (Table 2). Chromium was detected in side fish, Kuniran fish, Pepetek fish and Salem fish. Pb metal was not detected in fish tissue from all samples. Pb, Cd and As are non-essential metals. Cadmium metal indicates early enrichment, as well as very high total arsenic levels measured in all fish samples. The levels of non-essential metals cadmium and arsenic in some types of fish exceed the safe limits set by the National Standardization Agency. National Agency of Drug and Food Control (BPOM) regulations not provide safe levels of essential metals such as Cu, Cr and Se.
Table 2. Essential and non-essential metal from all samples (mg kg⁻¹).

| Location                      | Scientific Name | Local Name    | Water Content (%) | As    | Cd     | Cr     | Cu     | Pb     | Se     |
|-------------------------------|-----------------|---------------|-------------------|-------|--------|--------|--------|--------|--------|
| Palabuhan Ratu, Cimandiri     | *Psettodes* erumei | Sebelah 2     | 26.36             | 8.47  | 0.14   | 0.07   | 0.55   | 1.22   | 1.94   |
|                               | *Epinephelus* spilotoceps | Kerapu 2   | 23.80             | 3.49  | 0.07   | 0.43   | 0.14   | 0.55   | 1.43   |
|                               | *Elagatis* bipinnulata | Salem 3    | 20.97             | 4.20  | 0.09   | 0.07   | 1.70   | 2.60   | 4.56   |
| Karangsong, Cimanuk           | *Abalistes* stellatus | Etong 2        | 25.53             | 15.76 | 0.24   | 0.65   | 2.54   |
|                               | *Leiognathus* equulus | Pepetek 3   | 5.03              | 5.53  | 0.07   | 0.62   | 2.12   |
|                               | *Psettodes* erumei | Sebelah 3     | 24.39             | 2.89  | 0.04   | 0.14   | 1.53   |
|                               | *Upeneus* sulphureus | Kuniran 3    | 3.62              | 7.43  | 0.13   | 1.09   | 3.13   |

National Agency of Drug and Food Control/ BPOM (2018) 0.25 0.1 0.2
National Standardization Agency/BSN (2009) 1 0.1 0.3

Cadmium enrichment is supposedly sourced from the sediment, which was indicated by the high value of the enrichment factor [(EF) value > 1. For metal contamination of Cu, Cd, Pb and Zn in seawater, it is still in the normal category set by KMNKLH 2004 so that the potential for accumulation of seawater can be ignored [13]. Meanwhile, information regarding research on environmental conditions, especially heavy metals in the Cimandiri area, is still very limited. The main source of cadmium enrichment might come from anthropogenic activities, such as battery production, electrode components, plastic production and plant fertilizers [14].

Cd, Pb and As have a tendency to bioaccumulate so monitoring the quality of fishery commodities needs to be carried out regularly by relevant stakeholders. High total As levels were detected from all fish samples from both locations. Arsenic speciation in marine organisms exists in inorganic arsenic and organic arsenic known as arsenobetaine (AB). Arsenobetaine is usually found in aquatic organisms and less toxic than inorganic arsen [15, 16, 17]. In tuna and marlin, 95% of arsenic was found in arsenobetain (AB) [15]. Although the total measured arsenic levels exceed the limits set by SNI and BPOM, it should be noted that most of the arsenic in fish is in the organic arsenic (arsenobentain) which is relatively harmless compared to inorganic arsenic. Not all countries set safe limits for arsenic for fishery products. Indonesia, China, Malaysia, Thailand and Australia are some of the countries that have regulated limits on total arsenic contamination [7]. However, Indonesia has not regulated the speciation of arsenic in fish and fishery products due to the limitations of reference standards and sample preparation methods [15]. Sources of arsenic in the environment can come from natural or anthropogenic sources. Natural sources related to phosphate deposits and anthropogenic sources can come from the use of pesticides containing arsenic in the past or activities using phosphates [14].

Metal content in fish varies depending on the type of fish, nature of life and food. Metal content in demersal fish was generally higher than that of pelagic fish [18]. This is due to the living habits of these fish groups that are at the bottom or near the bottom of the water so that they are able to absorb...
heavy metals from the sediments around their habitat [19]. In addition, demersal fish are also generally a meat-eating group (carnivores), which are at a high trophic level [20]. The nature of fish in terms of food (herbivores, carnivores or omnivores) is highly dependent on the fish habitat, namely demersal, pelagic, or associated with corals, which in turn affects the position of the trophic level of an organism in the food chain [21]. The level of metal accumulation in biota is highly dependent on the trophic level, which the higher the position in the trophic level, the higher the magnification level.

Each fish studied in this study has a different trophic level (Table 1). The trophic level can be expressed in the form of numbers, generally for fish ranging from 2 to 5 [21]. The higher the value indicates the higher the level and position in the food pyramid. Based on this value, it is known that Etong fish, Pepetek and Kuniran are omnivorous fish and occupy second level consumers, while Salem fish and grouper fish are carnivorous, where their position in the food pyramid is the third level consumer. These differences in food types and trophic levels are known to affect the concentration of heavy metals in fish bodies [22, 23]. The safe limits set by the government for essential metal contamination such as Cu, Cr and Se in fishery products are not yet available. One of them is that there is no indication that essential metals harm organisms. Essential metals are known to function as cofactors for various enzymes that are important for marine organisms [24]. For the metabolic needs, essential and non-essential metals are sourced from water, food or sediment. However, these non-essential metals tend to be accumulated in tissues [25], in contrast to essential metals which have different metabolisms.

Metal accumulation in marine organism is influenced by many factors, such as metabolic needs, sex, and size [25]. However, the consistent relationship between metal content and fish size is still debated [25]. Research Yi & Zhang (2012) succeeded in detecting a positive correlation between metal levels of Cd, Cr, Cu, Hg, Pb, Zn with the size of the fish studied [26]. Karadede et al. (2004), coupled with a positive correlation between age and size of fish and bivalves in Oman and the total concentration of Hg [27]. This reinforces the fact that mercury is clearly stated to be able to bioaccumulate up to top predators [28]. Several studies also support a negative correlation between fish size and metal content in fish [29,30,31]. In this study, we cannot conclude clear correlation between metal and size because of sample size.

Metal accumulation in the fish will reach a steady state (balance) at a certain age [32]. This indicates that the essential metals (such as Cu and Zn) are dynamic, regulated and maintained at certain concentrations in the fish body. Metal accumulation in organisms is influenced by the rate of uptake, storage and elimination. The elimination rate in fish will decrease with increasing fish body size [33]. Thus, metals that have high uptake rates and low elimination rates will more easily accumulate in the network. Coupled with a decrease in metabolism as fish grows, so that metal exposure in the environment is higher than the maximum metabolic capacity limit of adult fish. This causes the condition to be seen as a positive correlation between body size (growth) and metal in tissues [26].

4. Conclusion
The levels of metals in fish from Cimanuk and Cimandiri indicate the potential for enrichment of Cd from anthropogenic sources. This condition is an indication of the need for monitoring in the aquatic environment around the fishing area. High levels of arsenic (As) in almost all fish samples cannot be used as a dangerous indication because most of the arsenic is found in the form of organic arsenic. Essential metals such as Se and Cu were found in varying levels in each type of fish, following the regulation of the fish body according to its metabolic activity.

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References

[1] Ministry of Maritime Affairs and Fisheries Indonesia September 2013
   http://pipp.djpt.kkp.go.id/profil_pelabuhan/1174/informasi

[2] World Health Organization 1996 Trace elements in human nutrition and health (Geneva: World
   Health Organization)

[3] Soegianto A, Moehammadi N, Irawan B, Affandi M and Hamami 2010 Cah. Biol. Mar. 51 1–8

[4] Mamboya F A 2007 Heavy metal contamination and toxicity. Studies of macroalgae from the
   Tanzanian Coast (Sweden: Stockholm University) p 49

[5] Inoue K I 2013 J. Clin. Toxicol. S 3 007

[6] Alonso M I, Montana F P, Miranda M, Castillo C, Hernandez J, and Beneditom J I 2004
   Biometals. 17 389-397.

[7] Pradianti O S, Rahayu W P and Hariyadi R D 2019 Jurnal Pascapanen dan Bioteknologi
   Kelautan dan Perikanan. 14 45-62

[8] Froese R and D Pauly 2019 FishBase World Wide Web electronic publication
   www.fishbase.org

[9] National Standardization Agency 2006 Indonesian National Standard No. 2354.2-2006
   Determination of water content in fishery product Jakarta, Indonesia.

[10] US EPA 2007 Method 3151a: Microwave assisted acid digestion of sediments, sludge, soils
    and oils https://www.epa.gov/sites/production/files/2015-12/documents/3051a.pdf

[11] National Agency of Drug and Food Control 2018 Regulation of the Drug and Food Supervisory
    Agency Number 5 of 2018 Maximum Limit of Heavy Metal Contamination in Processed
    Food Jakarta, Indonesia.

[12] National Standardization Agency 2009 Indonesian National Standard No. 7387: 2009 Maximum
    Limit of Heavy Metal Contamination in Food Jakarta, Indonesia.

[13] Harmesa, Lestari and Budiyanto F 2020 Oseanologi dan Limnologi di Indonesia. 5(1) 19-32

[14] Jaishankar M, Tseten T, Anbalagan N, Mathew B B, and Beeregowda K N 2014
    Interdisciplinary Toxicology. 7(2) 60–72

[15] Koesmawati T A, Buchari B, Amran M B, and Kardono L B S 2013 J App Pharm Sci. 3(07)
    116121

[16] Francesconci K A and Edmonds J S 1998 Croatica Chemica Acta. 71(2) 343-359

[17] Shiomi K 1994 Arsenic in the Environment. Part II: Human Health and Ecosystem Effects vol 27,
    ed J O Nriagu (New York: John Wiley & Sons, Inc) p 261–293

[18] Ahmad N I, Noh M F M, Mahiyyuddin W R W, Jaifar H, Ishak I, Azmi W N F W, Veloo Y and
    Hairi, M H 2015. Environ Sci Pollut Res. 22 3672-3686

[19] Naccari C, Cicero N, Ferrantelli V, Giangrosso F, Vella A, Macalus A, Naccari F and Dugo G
    2015 Bulletin of Environment Contamination and Toxicology. 95(5) 567-573

[20] Stergiou K I and Karpouzi V S 2002 Rev Fish Biol Fish. 11 217–254

[21] Joshi A, Desai AY, Kumar J, Saroj J and Tehsen P 2016 Environment and Technology. 5(3)
    1046-1056

[22] Agah H, Leermakers M, Elskens M, Fatemi M R and Baeyens W 2007 Water Air Soil Pollution
    181

[23] Astani E., Vahedpour, M. and Babaei, H 2016 Ecopersia. 4(3) 1517-1526

[24] Li Y, Liu H, Zhou H, Ma W, Han Q, Diao X and Xue Q 2015 Mar. Pollut. Bull. 97(1-2) 528–534

[25] Canli M and G Atli 2003 Environmental Pollution. 121 129–136

[26] Yi Y J and H Zhang 2012 Procedia Environmental Sciences. 13 1699–1707

[27] Karadede H, Oymak S A and Ünlü E 2004 Turkey. Environ Int. 30 183–8

[28] Soegianto A, Moehammadi N, Irawan B, Affandi M. and Hamamoi 2010 Cah. Biol. Mar. 51 1-8

[29] Guo J D 2005 Assessment of heavy metal concentration in several ocean endangered fauna
    Master thesis (Shangdong University)
[30] Farkas A, Salánki J and Specziár A 2003 *Water Res.* 37 959–64.
[31] García-Montelongo F, Díaz C, Galindo L, Larrechi M S and Rius X 1994 *Sci Mar.* 58 179–83
[32] Douben P E 1989 *Ecotox Environ Saf.* 18 35-58
[33] Trudel M and Rasmussen J 2006 *Canadian Journal of Fisheries and Aquatic Sciences.* 63 1890-1902