Heavy metals Cd and Cr found in sponges (porifera) at spermonde archipelago Zone II

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Abstract. Samalona and Barrang Lompo Islands are located in zone II of Spermonde Archipelago with the nearest distance is about 5 km from Makassar city beach. The close distance causes heavy metals as pollutants produced from activities in Makassar city and it surroundings to be carried out to zone II of Spermonde Archipelago waters. Marine biotas used as a bioindicator of heavy metals (Cd and Cr) pollution were sponges (Porifera). Analysis results by ICP-OES indicated that the largest quantities of the heavy metals (Cd and Cr) were found in sponge Xestospongia, i.e 1.250 mg/kg and 5.400 mg/kg dry weight, respectively.

1. Introduction

Heavy metals pollution sources can be divided into two, namely natural and human activity sources. Pollutions derived from nature can undergo rocks abrasion, rain, and landslide. Pollutions caused by human activities are much more common compared to those caused by natural processes. Human activities that produce wastes such as household waste, industrial waste, transportation, and agricultural activities can be pollution sources. The increased human population also contributes to the increase of domestic and industrial wastes introduced to the environment. This relates to increased needs such as foods, fuels, residences, and other primary needs, which will increase the volume of domestic and industrial wastes. The increased volume of domestic and industrial wastes that come into waters results in waters quality alteration.

Heavy metals pollution in Spermonde Archipelago waters can harm the life of organism which provides indirect impacts to human health. One of the primary characteristics of heavy metals is difficult to degrade, therefore they will accumulate in waters environment and their natural occurrence is difficult to breakdown. Secondy, they can accumulate in organisms including sponges, and thirdly they can accumulate easily in the sediment so that the concentration of accumulated metals is always higher than the metal concentration in the water column.

The persistent bioaccumulation of pollutants can be studied quantitatively by using sponges as biomonitors. This is based on the sponge ability as a filter feeder that can filter water 100-1200 mL per hour each gram. It has been reported that sponge communities can live in the same places and accumulate pollutants in long-term [1,2]. Sponges have a sophisticated cellular system, reproduction process and complex development, various feeding behaviors, ability to produce secondary metabolites with delicate biosynthesis pathways, and have cellular communication networks and close symbiotic relationship to other organisms [3]. Heavy metals and non-biodegradable chemical exhausts such as organochlorine compounds (pesticide wastes), organotin (antifouling paint waste), and hydrocarbon polycyclic aromatic (oil and gas wastes) are contaminants persistent in the waters
environment [4]. The existence of these contaminants in the concentration above the threshold level can be toxic to marine organisms and have an adverse effect on ecosystem quality [5,6].

2. Results
Sessile invertebrates are ideal organisms to be used as bioindicators because of their high adaptability to environmental changes due to low mobility, so that their abundance or absence can provide a description of general ecological conditions, composition and structure of their communities are not affected by the presence of migration and local movement, in their attempt to defend their self from predation, sponges produce “chemical weapon” in which the biosynthetic process is affected more by the environmental physical condition compared to ecological interaction among their own types [7,8].

The results of the physical and chemical parameters of waters in three sampling zones can be seen in Table 1.

| Condition | Samalona | Barrang Lompo |
|-----------|----------|---------------|
| Temperature (°C) | 29 | 28.6 |
| Salinity (‰/oo) | 34 | 31 |
| pH | 6.8 | 7 |

Physical and chemical parameters (Table 1) have met the requirement for sponge growth. The optimum temperature for sponge growth is 25-29°C. Bioaccumulation depends on the temperature in which metal concentration accumulates increasingly with temperature. The temperature effect is presumed to involve the mechanism of ion transport on the membrane surface. The salinity of waters for the three islands also met the requirement for sponge growth (29-36 ‰/oo). Generally, biotic metal concentration increases with the decrease of the salt level. The different salt levels can cause different metal absorption rate due to a physiological change in living organisms such as drinking rate or water filtration rate. Waters environmental pH that meets the requirement for sponge growth range from 6 to 8 and affects the development of new metal species in the water. pH effect also depends on the types of metal.

2.1. Analysis Results of Heavy Metals (Cd and Cr) in Sponge using ICP-OES
Data on analysis of Cd in sponges using ICP-OES can be seen from Figure 1.

![Figure 1. Graphic of Cd concentration in sponges (Porifera)](image-url)
Data on analysis of Cr in sponges using ICP-OES can be seen from figure 2.

![Figure 2](image2.png)

**Figure 2.** Graphic of Cr concentration in sponges (Porifera)

2.2. *Analysis Results of Heavy Metals (Cd and Cr) in Sediment and Seawater using ICP-OES*

Data on analysis of heavy metals (Cd and Cr) in sediment using ICP-OES can be seen from figure 3.

![Figure 3](image3.png)

**Figure 3.** Graphic of Cd and Cr concentrations in sediment

Data on analysis of heavy metals (Cd and Cr) in sediment and seawater using ICP-OES can be seen in Figure 4.

![Figure 4](image4.png)

**Figure 4.** Graphic of Cd and Cr concentrations in seawater
3. Discussion

The highest Cd concentration accumulated in sponges was obtained from *Melophlus sarassinorum* (2.050 mg/kg) in Barrang Lompo Island, *Xestospongia* in Barrang Lompo Island accumulated heavy metal Cd with the lowest concentration compared to other sponge species. Sponges are biota that are the potential to be contaminated heavy metals because of their character as a filter feeder. Protein and amino groups are easy to bind to Cd. Protein and amino groups have S, N, and O atoms having free electron pairs which are very favorable to bind to metal ions. Cadmium can form cadmium halide, cadmium sulfide, cadmium oxide, and organo-cadmium compounds. The solubility of the cadmium compounds depends on seawater pH.

Pollutant metals absorbed from waters to sponge body take the route through several cell membranes consisting of the biomolecular layer formed by lipid molecules and protein molecules distributed in entire membranes. Heavy metals get into the membrane through passive diffusion and active transport, depending on their compounds type. When present inside the cells, metals will form complex and ligand. Heavy metals can bind to sulfhydryl, hydroxyl, carboxyl, imidazole, and amino groups from protein. Heavy metal ions are the most effective to bind to sulfhydryl groups, such as cysteine, with molecule structure having nitrogen groups, like those present in lysine and histidine. The attack on the sulfide bond in protein will damage the protein [9].

Study findings indicated that cadmium and chromium have a higher concentration in sediment compared to that in seawater. The highest cadmium and chromium concentration was obtained from Samalona Island. Accordingly, the highest cadmium concentration in seawater was obtained from Samalona Island. Seawater derived from Barrang Lompo Island contain a higher chromium compared to Samalona Island.

When the industrial waste gets into water, sedimentation will occur inside the sediment. Some of the heavy metals attach to particles which were then precipitate and accumulate in sediments. The heavy metals dissolved in water will move to sediment when bind to the free organic material or organic materials lining the sediment surface, and direct attach by sediment particle surface.

The solubility of chromium depends on salinity. Hexavalent chromium and trivalent chromium are toxic to marine biota. Chromium precipitation can be caused by alkaline pH, forming hydroxide, oxide, and carbonate which are insoluble. Cr is an essential trace element. In seawater, Cr occurs in the form of oxyanion CrO$_4^{2-}$ or Cr$_2$O$_7^{2-}$) or reduced Cr$^{3+}$.Cr(VI) can be absorbed, generally through the reduction-precipitation process, ion exchange, and reverse osmosis [10]. Although Cr (VI) as chromate is known to cause mutagenicity and even carcinogen due to its ability in damaging the cell walls, this metal can be proposed as essential metal in its oxidized form (Cr$^{3+}$), the most stable form in water.

Environmental conditions can also be measured using a biomarker, indicators that can provide information on biochemical, physiological, and histochemical changes in organisms due to xenobiotic exposure (toxic compound). Sponges can be used as an indicator because they are filter feeders that can filter water with a volume of 100-1200 mL per hour each gram. Sponges community can live in similar sites and accumulate pollutants in long-terms [11,12]

4. Conclusion

Sponges that can accumulate the highest Cd and Cr (2.050 mg/kg and 5.400 mg/kg) from the environment are *Melophlus sarassinorum* and *Xestospongia* from Barrang Lompo Island. The highest Cd and Cr concentration in sediment were derived from Samalona Island, 1.000 mg/kg and 1.700 mg/kg, respectively.

Seawater contains metal concentration which is not equal to sponge and sediments, because of its dynamic characteristic. Cd concentration in seawater of Samalona Island provided the highest result (0.009 mg/kg). The highest Cr concentration (0.0548 mg/kg) was obtained from the seawater of Barrang Lompo Island.
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