The Ability of Ferns to Accumulate Heavy Metals (Hg, Pb And Cd) In The Waters of The Gorontalo River

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Abstract
Sustainable development can be caused by more human’s activity. This activity, it will have an impact on the surrounding environment which can disrupt the stability of the ecosystem, one of which is the river water ecosystem. The research aims to determine the ability of ferns in accumulating heavy metals so that they can be used as indicators of the depletion of river waters ecosystem environments and can be used as fitoremediant areas of waters which accumulate heavy metals. This research is descriptive quantitative. Retrieval of initial data or sample in this study used survey methods and random sampling techniques, testing samples by using the Ranger X-ray Fluorencie (XRF) method. Based on the results of the study that, ferns can accumulate heavy metals, the parts that accumulate are located below the root surface and above the soil surface, namely stems and leaves. In the roots have more amount in accumulating heavy metals than in the stem and leaves, this is because the metal is indicated on the soil. From these results, it can be concluded that ferns can be used as water purification plants in river ecosystems that are indicated by heavy metals.

Introduction
Bone Bolango Regency is a division of Gorontalo Regency which is in one unit of Gorontalo Province. Bone Bolango Regency was formed based on Law Number 6 of 2003 and was officially established on May 16, 2003. Bone Bolango Regency has an area of 1,984.54 Km² or 16.24% of the total area of Gorontalo Province. The area of Bone Bolango Regency is located between 09° - 01°15' North Latitude and 121°84’ - 123°26’ East Longitude. Bone Bolango Regency has a mineral potential that is traditionally managed by the general public.

Mining activities in the bone bolango district are estimated to be around 2,112 miners. In addition, the mining results obtained are still in the form of a mixture of materials and then use drum for the process of destruction of the material. This process is to facilitate the processing of gold which is still integrated with the material. To separate the gold, the material inserted into the drum is mixed with mercury which works as a gold binder. Tromol is placed very close to the river so that the waste from the drum goes
directly to the river body. This waste discharge causes pollution of heavy metals into the aquatic environment. In addition to gold processing there are several other activities that cause polluted aquatic ecosystems such as workshops, agriculture and household activities as well as the use of pesticides and herbicides in the process of eradicating pests, this can result in the deposition of heavy metals into sediments and then into the aquatic environment through infiltration or percolation.

In these processing and implementing activities of environmental quality standards are absolutely necessary to ensure the stability of the river ecosystem. Disposal of special gold mining processing wastes that are managed traditionally contain heavy metal elements such as (Hg, Pb and Cd) which can pollute the river environment and ultimately affect the life of flora and fauna, threatening the diversity of species and their ecosystems. The river is a living environment that provides important life for living things, which have high diversity and resources. The river resources will continue to be maintained and stable if there is no ecological pressure in them, which is caused by human activities that use resources excessively which results in changes in the river's ecological system. River pollution, which is one form of pressure from human activities that is directly carried out in the river, as well as human activities on land against the river environment and the resources therein can cause harm to natural systems (ecosystems) that have been arranged previously and for humans that are part of the system natural.

Human activities in utilizing resources often produce pollutant waste which can endanger life in the river flow. Increasing human activities around river flows can cause changes in these aquatic ecosystems. On the other hand, the threat of the preservation of biodiversity, in the form of a decline in population and plant species continues, which is caused by human activities. (Irawanto, 2014). These activities can trigger changes in aquatic ecosystems because they can produce heavy metals such as mercury (Hg), lead (Pb) and cadmium (Cd) which are not needed by organisms.

The presence of heavy metals such as mercury (Hg) into the aquatic environment does not interfere with these aquatic ecosystems, but it is very dangerous if the heavy metals enter the plant's body. The entry of heavy metals into plant growth will disrupt all plant tissue systems so that it will cause khorosis and necrosis even death. According to (Forstner and Wittman, 2001). Heavy metals in the food chain system cause bioaccumulation of heavy metals in the organism's body in the food chain system. Bioaccumulation is the process of increasing the concentration of heavy metals in the body of living things according to the level of the food pyramid and the higher the tropical structure of one type of organism in the food chain the greater the level of heavy metals contained in the organism's body.

One of the biotic components in the food chain in river ecosystems is ferns (Pteridophyta) which are biotic components in the food chain in river ecosystems that are very tolerant of water pollution. It is known that there are types of ferns which are used as ingredients of vegetables consumed by the general public of Gorontalo, namely types of Pteridium aquilinum. Anthony et al. (2007) suggested that there were 10 types of ferns that could be used as hyperaccumulators, namely Adiantum aethiopicum, Blechnum cartilagineum, Blechnum nudum, Cheilanthes nitida, Dennstaedtia davallioides, Doodia aspera, Nephrolepis multiflora, Pellaea falcata, Pteridium aquilinum and arsenic (As) hyperaccumulating Pteris vittata. The ability of ferns to accumulate heavy metals, significantly more accumulated to the roots of leaves, shows limited mobility and heavy translocations absorbed by ferns. Absorption of heavy metals causes plants to continue
to grow unhindered and is an important means of heavy metal tolerance (Ernst et al. 1992), but can cause death if the toxicity has crossed the threshold (Baker et al. 2000).

**Materials and Methods**

This research is descriptive quantitative. The method used in this study is the roaming method. This is intended to facilitate data collection of ferns (Pteridophyta) found in the vicinity of the Bone River and the Tombulilato River Stream.

The way of sampling plants, carried out by using hands and shovels, to maintain the authenticity and quality of plant samples stored in thick plastic, then the sample is taken to a biology botanical laboratory for preparation of plant samples, after that, the samples are washed until the water has not changed and finally washed by using distilled water. Processing of plant samples is carried out by each plant species so that it can be distinguished, then cut into small pieces and wrapped in allium foil and labeled on each organ of the species then put into the oven at 400°C until it gets a constant weight. Then weighed again the dry weight of the plant and then mashed facilitate analysis and then to examine the content of heavy metals using the X-ray Flourenceice (XRF) S2 Ranger.

**Data Analysis**

Identification of ferns is carried out in a biology laboratory by describing the morphological characteristics of plant species obtained from two river streams. Each type of plant found is described in its taxonomic hierarchy, identification of ferns is carried out at the Biological Laboratory of Gorontalo State University, using key books such as Stenis (2008), Hidayat (2011) and P.S. Short & D.J. Dixon, (2011). Analysis of levels of heavy metal Mercury (Hg) in ferns (Pteridophyta) was carried out at the Gorontalo State Physics Laboratory using X-ray Flourenceice (XRF) S2 Ranger. The results of the analysis are obtained in table form.

**Results and Discussion**

Based on the results of the study found 5 types of ferns (Pteridophyta) found around the river flow namely Pteridium revolutum, Cyclosorus interruptus, Pityrogramma calomelanos, Cheilanthes nitida and Nephrolepis multiflora.

**Table 1. Fern species around the river basin.**

| No | Type Ferns (Pteridophyta)       | Bone River | Tombulilato River |
|----|--------------------------------|------------|-------------------|
|    |                                | ST 1 | ST 2 | ST 3 | ST 1 | ST 2 | ST 3 |
| 1  | *Pteridium revolutum*           | √    | √    | √    | √    | √    | √    |
| 2  | *Cyclosorus interruptus*        | √    | √    | -    | -    | -    | -    |
| 3  | *Pityrogramma calomelanos*      | √    | √    | √    | √    | √    | √    |
| 4  | *Cheilanthes nitida*            | √    | √    | √    | √    | √    | √    |
| 5  | *Nephrolepis multiflora*        | √    | √    | √    | √    | √    | √    |
Table 2. The content of heavy metals (Hg, Pb and Cd) contained in the organs of ferns (Pteridophyta), at Station I of the River Bone, and the River Tombulilato.

| No | Location       | Type Ferns (Pteridophyta) | The average content of heavy metal in ferns (Pteridophyta) | Root (ppm) | Stem (ppm) | Leaf (ppm) |
|----|----------------|---------------------------|----------------------------------------------------------|------------|------------|------------|
|    |                |                           | Hg  | Pb  | Cd | Hg  | Pb  | Cd | Hg  | Pb  | Cd |
| 1  | Bone River     | Pteridium revolutum       | 0.30| 246 | 160| 0.30| 250| 235| 0.23| 270| 247|
|    |                | Cyclosorus interruptus    | 0.31| 158 | 143| 0.28| 145| 122| 0.20| 142| 135|
|    |                | Pityrogramma calomelanos  | 0.26| 157 | 147| 0.21| 156| 139| 0.18| 168| 154|
|    |                | Cheilanthes nitida        | 0.33| 352 | 276| 0.31| 243| 356| 0.30| 266| 342|
|    |                | Nephrolepis multiflora    | 0.32| 123 | 223| 0.26| 223| 212| 0.22| 243| 345|
| 2  | Tombulilato to River | Pteridium revolutum       | 0.05| 134 | 124| 0.04| 141| 132| 0.02| 121| 154|
|    |                | Pityrogramma calomelanos  | 0.05| 189 | 179| 0.04| 111| 98 | 0.03| 114| 111|
|    |                | Cheilanthes nitida        | 0.20| 178 | 230| 0.15| 199| 265| 0.12| 173| 278|
|    |                | Cyclosorus interruptus    | 0.04| 156 | 189| 0.02| 103| 165| 0.03| 150| 245|

Table 3. The content of heavy metals (Hg, Pb and Cd) contained in the organs of ferns (Pteridophyta), at Station II of the River Bone, and the River Tombulilato.

| No | Location       | Type Ferns (Pteridophyta) | The average content of heavy metal in ferns (Pteridophyta) | Root (ppm) | Stem (ppm) | Leaf (ppm) |
|----|----------------|---------------------------|----------------------------------------------------------|------------|------------|------------|
|    |                |                           | Hg  | Pb  | Cd | Hg  | Pb  | Cd | Hg  | Pb  | Cd |
| 1  | Bone River     | Pteridium revolutum       | 0.35| 359 | 165| 0.31| 368| 265| 0.33| 387| 127|
|    |                | Cyclosorus interruptus    | 0.30| 368 | 345| 0.32| 477| 387| 0.36| 327| 399|
|    |                | Pityrogramma calomelanos  | 0.32| 365 | 178| 0.34| 334| 343| 0.30| 311| 122|
|    |                | Cheilanthes nitida        | 0.31| 434 | 346| 0.36| 376| 389| 0.30| 387| 392|
|    |                | Nephrolepis multiflora    | 0.32| 267 | 227| 0.25| 235| 233| 0.24| 245| 367|
| 2  | Tombulilato to River | Pteridium revolutum       | 0.18| 247 | 189| 0.14| 198| 100| 0.11| 256| 121|
|    |                | Pityrogramma calomelanos  | 0.17| 200 | 120| 0.12| 290| 156| 0.15| 256| 179|
|    |                | Cheilanthes nitida        | 0.14| 298 | 189| 0.13| 367| 180| 0.11| 293| 104|
|    |                | Cyclosorus interruptus    | 0.06| 202 | 126| 0.03| 278| 179| 0.05| 208| 137|
Table 4. The content of heavy metals (Hg, Pb and Cd) contained in the organs of ferns (Pteridophyta), at Station III of the River Bone, and the River Tombulilato.

| No | Location          | Type Ferns (Pteridophyta)          | The average content of heavy metal in ferns (Pteridophyta) |
|----|-------------------|------------------------------------|----------------------------------------------------------|
|    |                   |                                    | Root (ppm) | Stem (ppm) | Leaf (ppm) |
|    |                   |                                    | Hg     | Pb     | Cd     | Hg     | Pb     | Cd     | Hg     | Pb     | Cd     |
| 1  | Bone River        | Pteridium revolutum                | 0.33   | 423    | 465    | 0.30   | 469    | 352    | 0.34   | 326    | 433    |
|    |                   | Cyclosorus interruptus             | 0.30   | 398    | 322    | 0.32   | 377    | 367    | 0.37   | 427    | 387    |
|    |                   | Pityrogramma calomelanos           | 0.31   | 475    | 376    | 0.32   | 344    | 337    | 0.32   | 411    | 310    |
|    |                   | Cheilanthes nitida                 | 0.31   | 483    | 323    | 0.27   | 445    | 321    | 0.30   | 455    | 356    |
|    |                   | Nephrolepis multiflora             | 0.32   | 377    | 267    | 0.30   | 398    | 241    | 0.34   | 340    | 360    |
| 2  | Tombulilato River | Pteridium revolutum                | 0.07   | 251    | 289    | 0.03   | 276    | 276    | 0.05   | 260    | 210    |
|    |                   | Pityrogramma calomelanos           | 0.08   | 176    | 230    | 0.06   | 387    | 278    | 0.06   | 241    | 220    |
|    |                   | Cheilanthes nitida                 | 0.11   | 293    | 181    | 0.10   | 243    | 251    | 0.09   | 276    | 203    |
|    |                   | Cyclosorus interruptus             | 0.07   | 193    | 220    | 0.04   | 214    | 292    | 0.05   | 190    | 125    |

Heavy Metal Content in Nail Plants (Pteridophyta) in the Bone River Region and Tombulilato River

Based on the results of the analysis carried out at the Gorontalo State Physics Laboratory, using the Ranger S2 Fluorecence X-ray (XRF) testing method. The samples analyzed were ferns (Pteridophyta) which were taken directly around the Bone river and Tombulilato river Bone Bolango District. Based on the results of the analysis show that the river is polluted by heavy metals (Hg, Pb, Cd) as seen in the Heavy metal content table.

From the results of the research, there were 5 types of ferns (Pteridophyta) which could accumulate heavy metals (Hg, Pb and Cd), namely Pteridium revolutum, Cyclosorus interruptus, Pityrogramma calomelanos, Cheilanthes nitida and Nephrolepis multiflora. Based on the results of analysis of heavy metal levels in ferns (Pteridophyta) that river waters are indicated by heavy metals. The presence of heavy metals around river waters cannot be avoided because it is a place for community activities ranging from gold processing, agriculture and household activities. These activities cause the presence of heavy metals in river waters. As one example, gold processing around the river uses mercury in the amalgamation process. Activities that cause heavy metals in river waters due to direct waste from drum and river then settle into sediments. Heavy metals found in sediments greatly influence the heavy metal content in plants that grow above them, so that high or low metal content in the sediment will reflect metal content in plants, Darmono (1995). The heavy metal content in plants is also influenced by sedimentation (Palar, 2012). According to Hernandez
et al (2010) waste originating from mining extracts that enter into soil containing Pb and Cd heavy metals is more than 1500 mg/kg-1. Malar et al (2014) suggested that contaminated wasting water containing heavy metal Pb around 1000 mg / l can be seen if plants have shown symptoms of chlorosis. According to Cheng (2003) when plants show chlorosis, the plant has accumulated Cd and Pb heavy metals in excess of 800 mg / kg. Then confirmed by Malar et al (2014) plants experiencing symptoms of chlorosis have accumulated heavy metals Cd and Pb 100-1000 mg/l. In addition, the high content of heavy metal lead (Pb) and cadmium (Cd) detected in ferns, due to corrosive from rock excavations in the mining area so that heavy metals in the rocks are carried away by the rain and head to the river. According to Palar (2004) heavy metals can occur due to rock blasting which is then carried by rain to the river through a run-off process. Another factor is the result of the use of pesticides and herbicides by farmers as pest control. According to Tangahu et al (2011), that the content of heavy metal lead (Pb) found on herbicides and pesticides reaches 1100 mg/m3. Then this is reaffirmed by Malar et al (2014) that pesticides can cause high accumulation of heavy metals into the sediment.

Apart from the sources discussed earlier, motorized vehicles are also one of the main sources of pollution because they contain various pollutants which are harmful to humans, animals, plants. According to Fergusson (1990) pollutants (pollutants) originating from motor’ vehicle gases are generally in the form of combustion gases and heavy metal particles such as lead (Pb). Black lead (Pb) released from motorized vehicles averages 0.02-0.05 µm in size. The smaller the particle size the longer it stays. If it is observed along river waters starting from the eastern Suwawa sub-district to the Botupingge sub-district, the highway is close to the Bone River. The amount of heavy metals in the environment is strongly influenced by the volume or density of traffic, distance from the highway, and engine acceleration and wind speed.

The presence of heavy metals in the environment is strongly influenced by environmental factors such as acidity, current velocity, turbidity, dissolved oxygen and salinity. According to Palar (2004) the normal acidity (pH) of water is between 6-8. If the pH value is below or above the normal value, the environmental conditions of the waters have been polluted, the lower the pH value, the greater the accumulated heavy metal content or vice versa the higher the pH value, the greater the heavy metal content. Based on the measurement results of dixolved oxygen (DO) then, the Bone river and the Tombulilato river are in the moderate polluted category. according to Supardi, (1984) water pollution is divided into 3 parts, namely lightly polluted if DO levels = 5 mg/L, medium polluted if DO levels are between 2-5 mg / L and heavily polluted if DO levels are between 0, 1 - 2 mg/L. Based on data from (Balirsti Gorontalo Province, 2014) that the Bone river has been moderately polluted in the upstream part (Suwawa Timur District, Dumbaya Bulan Village) and lightly polluted in the lower part (Bendungan, Suwawa Tengah District).

The existence of heavy metals in the environment will endanger the life of living things and be more dangerous if they enter into the metabolic system of living things in excess of the boundary limit. Plants that are able to accumulate heavy metals in their bodies are called accumulator plants. Hernandez et al. (2010) that plants that are hyperaccumulators if they are able to accumulate heavy metals more than 1000 mg/kg. Then confirmed by Landis, et al. (2011) if the accumulation ability is as much as 100 ppm or more than 1000 mg / kg dry weight is considered to be a hyperaccumulator plant. Draghiceanu et al. (2014) my plants are hyperaccumulators if they are able to accumulate more than 1,000 mg/kg cadmium (Cd) and
10,000 mg/kg lead (Pb). So that ferns are potential plants as hyperaccumulators. As with other aquatic plants used in phytoremediation (Tangahu, 2011).

Conclusions
From the results of the discussion, it can be concluded that there are 5 types of ferns on the Bone River, namely Pteridium revolutum, Cyclosorus interruptus, Pityrogramma calomelanos, Cheilanthes nit and Nephrolepis multiflora, while the river Tombulylate has 4 types of ferns namely Pteridium revolutum, Pityrogramma calomelanos, Cheilanthes nitid and Nephrolepis multiflora. The presence of ferns in each region is strongly influenced by climatic conditions, thus affecting the accumulation of heavy metals in ferns. Heavy metal levels (Hg, Pb, Cd) found in ferns (Pteridophyta) in river waters are very dangerous. This can disrupt the ecosystem inside and can break the food chain in the ecosystem. These activities are in the form of gold processing which the waste is discharged into the river, the use of herbicides and pesticides in eradicating pests that settle into sediments and into the river through infiltration, workshop which removes the remaining oil into the ditch / ditch which then goes to rivers and discarded household waste to the river. All of these activities are the main sources of heavy metals which can pollute the river environment including living organisms in the waters and people who use the river as a livelihood. Therefore the right solution to remediate land contaminated with heavy metals due to human activities can use ferns as fitoremediant.

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