FITOACUMULATION OF Mn AND Fe ON NYPA FRUTICANS IN TALLO RIVER, MAKASSAR

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Abstrak. Penelitian tentang fitoakumulasi Mn dan Fe dalam tumbuhan nipah (Nypa fruticans) dilakukan dengan tujuan untuk mengetahui potensi fitoakumulasi tumbuhan Nypa fruticans di Sungai Tallo. Sampel diambil pada air, sedimen, akar, pelepah, dan daun di lima titik sampling yang mewakili area tercemar oleh aktivitas kawasan industri dan pemukiman masyarakat. Sampel air didestruksi dengan HNO3 pekat, sedangkan sampel sedimen didestruksi kering dengan Na2CO3 dan NaHCO3, kemudian dilarutkan dengan akuaregia dan sampel bagian tumbuhan didestruksi basah dengan HNO3 6 M dan H2O2 pekat dan dianalisis menggunakan ICP EOS Shimadzu 9000. Hasil analisis menunjukkan bahwa Nypa fruticans mampu mengakumulasi Mn dan Fe, selain itu kemampuan akumulasinya menunjukkan bahwa secara alami tumbuhan ini hiperakumulator terhadap Fe namun tidak hiperakumulator terhadap Mn. Berdasarkan hasil perhitungan BCF dan TF, maka mekanisme fitoakumulasi Nypa fruticans terhadap Mn dan Fe adalah fitostabilisasi.

Kata kunci: Mn, Fe, nipah, fitoakumulasi, hiperakumulator.

Abstract. The phytoaccumulation of Mn and Fe in nipah palm (Nypa fruticans) has objective to find out the phytoaccumulation potential of Nypa fruticans in Tallo river. Samples were taken in water, sediments, roots, midribs and leaves at five sampling spots representing polluted areas by activities of industrial estates and community settlements. Water was destructed by concentrated HNO3, meanwhile sediments were destructed by dry destruction with aquaregia and plant tissues were destructed by wet destruction with HNO3 6 M and concentrated H2O2, then all the samples were carried on analysis using ICP EOS Shimadzu 9000. The result of analysis has shown that Nypa fruticans was able to accumulate Mn and Fe, moreover the accumulation potential indicated Nypa fruticans able to be natural hyperaccumulator for Fe, otherwise to Mn. According to BCF and TF result were shown the mechanism of phytoaccumulation in Nypa fruticans for Mn and Fe as phytostabilization.

Keywords: Mn, Fe, Nypa fruticans, phytoaccumulation, hyperaccumulator.

INTRODUCTION

The industry is one of economic development that increases regularly and very promising a better future for the community economy (Widowati, et al, 2008). The development of the industrial sector provides a positive impact in the form of the expansion of employment and increased incomes, while disruptive is the high rate of change of land use which is not in accordance with the rules of ecology, urbanization is less controlled, high population growth, as well as the pollution of waters due to the disposal of wastewater that goes beyond the threshold (Setiawan, 2014). Various human activities such as the remaining results of domestic waste and agriculture provide a negative impact on the area of the estuary and coast (Kariada and Irsadi, 2014).

The management of waste containing heavy metals, especially liquid waste conventionally start perceived ineffective and difficult. Therefore needed some alternative waste treatment liquid and effective use of environmentally friendly technology. One way of processing is to use aquatic plants that have the ability to absorb and accumulate heavy metals (Juhaeti, et al., 2004). The diversity of endemic plant species that exist in Indonesia is very high. Types of flora that belong to Indonesia very much has the potential to reduce pollution from contaminated environments in this aquatic plants, one of which is the mangrove plant or the like. Indonesia as one of the countries with extensive mangrove forest is the world's largest or the like (Juhaeti et al., 2004).

Tallo River is located in the northern side of the Makassar city experienced high pressure due to the existence of settlements, industrial areas of Makassar (KIMA), PLTU, farming and agriculture (Setiawan, 2014). Existing industries around the river causing Tallo River polluted by industrial wastes. Heavy metal waste is one of the polluters in the river Tallo.

Station 1 is located on the East side of the Perintis Kemerdekaan street near the area of bridges between Perintis Kemerdekaan street and Dr. Leimena street. Station 2 is located in the vicinity of the bridge after Perintis Kemerdekaan Road and PLTU Makassar toward the Kera-Kera dock. Station 3 is located around the Delta Lakkang towards Sinri Jala. Station 4 is located in Pampang River. Station 5 is located at the t-junction Sinri Jala leading to the coastal town of Makassar.

The position of the specified stations is representatively determined based on the situation and conditions in Tallo River, which can represent the points of the existing pollution. Sampling was done on a five-point, namely:

1. The station 1 is located at the coordinates S 5º8' 37.904" and E 119º28'45.737"
2. Station 2 is located at the coordinates S 5º8'40. 366 "and E 119º28'22.496"
3. Station 3 is located at the coordinates S 5º7'20.723 "and E 119º27'39.349"

4. Station 4 is located at the coordinates S 5°8'22.902 "and E 119°26'42.684"
5. Station 5 is located at the coordinates S 5°6'53.650 "and E 119°26'59.092"

Sample of sediment, water, and plant parts of Nipah (*Nypa fruticans*) were acquired in July 2018.

Figure 1. Map of Sampling Location

MATERIAL AND METHODS

Tools

The tools used in this research are GPS, eckman grab, water sampler, sample bag, ice box, cutting tool, oven SPN 150 SFD, Ohaus AP balance sheet 110, hot plate, ICP EOS Shimadzu 9000, porcelain cup, measuring flask, cup, funnel, and volume pipette.

Materials

The materials used in this study are water from rivers, sediments, roots, midribs, and leaves Nypa fruticans obtained from around the river Tallo, aquabidest, HNO_3 (Merck), H_2O_2 (Merck), aquaregia, standard-element 50 ppm (Merck), Na_2CO_3 (Merck), $NaHCO_3$ (Merck), and Whatman filter paper No. 42.

Procedures

Sample Preparation

Samples of river water taken in the field and moved into polyethylene bottles, then added to 5 mL of concentrated HNO_3, then stored in the icebox. River water samples were destructed by 5 mL of concentrated HNO_3 then were evaporated to 10 mL on hot plate, then samples were filtered into 50 mL measuring flask with aquabidest pH 2. Samples were homogenized then analyzed by ICP.

Samples of sediments that have been taken in the field then dried at 105 °C in the oven. Sediment that has been dried, destructed by weighing 2.5 g Na_2CO_3 into a porcelain cup and then added 0.5 g sediments and added more 2.5 g of $NaHCO_3$ to cover samples of sediment, and then the samples were inserted into the furnace and heated at 850 ^{o}C for ± 3 hours. Aquaregia was added to dissolve the destructed samples, then the samples were filtered into 50 mL measuring flask and then diluted to the line on the flask with aquabidest pH 2. Samples were homogenized then analyzed by ICP.

Each sample of root, stem and leaves washed with distilled water then dried at 80-85 °C in the oven. Sample of root, stem and leaves have dried then crushed with a mortar. Each of the fine samples carefully weighed 0.5 g into a 100 mL beaker and added 15 mL of HNO_3 6 M and 5 mL of H_2O_2 (p), then samples were heated at 60-80 °C until the volume becomes ± 1 mL, then filtered into 50 mL measuring flask and diluted with aquabidest pH 2. Samples were homogenized then analyzed by ICP.

Standard solutions were prepared from multielement 50 ppm into a series of solutions of the standard raw Mn and Fe using akuabidest pH 2 with a series of 0.01 ppm; 0.05 ppm; 0.1 ppm; 1 ppm; 3 ppm; 5 ppm and 10 ppm.

Determination of the Metal Concentration

Concentrations of the metals obtained from the results of the analysis using ICP is calculated using the following equation:

$$C = \frac{a \, x \, V \, x \, fp}{g}$$

Where:

C = actual concentration
a = concentration from the results of ICP analysis
V = sample volume
fp = dilution factor
g = sample mass

The Determination of Mechanism of The Absorption of Heavy Metals

Concentration of the sample analysis as the data was processed by the formula of determining the value of the Translocation Factors (TF) and Bioconcentration Factors (BCF). Determination of heavy metal accumulation mechanism has been formulated by Ghosh and Singh (2005) as follows:

$$\text{TF} = \frac{[M] \; in \; leaf \; (mg/kg)}{[M] \; in \; root \; (mg/kg)} \; x \; 100\%$$

$$\text{BCF} = \frac{[M]\ average\ in\ plants\ tissue\ (mg/kg)}{[M]\ contained\ in\ sediments\ (mg/kg)}$$

BCF and TF values are used to determine the mechanism of the absorption of metals by plants. According to the Liong, et al., (2010), it is phytostabilization mechanism if the value of the BCF > 1 and TF < 1, whereas the mechanism is phytoextraction if the BCF < 1 and TF > 1.

RESULTS AND DISCUSSION

The Concentration Of Heavy Metals In River Water

1. Manganese

River area is often polluted by heavy metals. Mn is one of heavy metals which contained in the wastewater from industrial areas that are usually not treated well and development activity that disposes of domestic waste into the river can diminish the water quality of the river (Judo, 2006). The results of the analysis of the Mn in the river water in the river Tallo is shown in table 1.

Table 1. Mn Concentration in water of Tallo River

Location	Concentration (mg/L)
Station 1	167,05
Station 2	140,65
Station 3	135,85
Station 4	160,05
Station 5	161,55

The results of the analysis showed concentrations of Mn in river water at all stations. Station 1 has the highest concentration of Mn, it was caused by the presence of zinc factory and PLTU, both these companies use Mn compound in their industrial activity, in addition there is road construction activities as well. Likewise with station 4 and 5 that are close to residential communities and Makassar Industrial Area. The magnitude of the concentration of Mn in the river water has passed through the limits of tolerance metal Mn in river water based on Surface Water Regulation of EU Directive Regulation by the Environmental Protection Agency which is 1 mg/L.

2. Ferrum (Iron)

Source river water pollution can come from a variety of types of waste such as industrial waste, domestic waste, as well as other activities such as agriculture, fishing, and tourism. The level of pollution of river became increasingly high with increasing amounts of pollution load entering the waste stream and also due to the decreasing river flow discharge (Judo, 2006). The results of the analysis of Fe in the river water in the Tallo River is shown in table 2.

Table 2. Fe Concentration in water of Tallo River

Location	Concentration (mg/L)
Station 1	39,60
Station 2	16,15
Station 3	15,85
Station 4	41,60
Station 5	41,80

Data in table 2 shows the highest concentration of Fe is at station 5 which is the point of confluence of the Pampang River and Tallo River. Station 1 is located near PLTU and zinc factory, while the Station 4 is situated in Pampang River that is contaminated from development activity. The magnitude of Fe concentration in river water has passed through the metal tolerance limit of Fe in river water based on Surface Water Regulation of EU Directive Regulation by the Environmental Protection Agency which is 2 mg/L.

The concentration of heavy metals in Sediment

1. Manganese

Manganese liquid waste which precipitates to form sediments derived from industrial which uses Mn compounds for processing waste water and using Mn in matchsticks, batteries, and other community activities that can increase the concentration of Mn in sediments (anonymous, 2003). The results of the Mn analysis of the sediment in Tallo River is shown in table 3.

Table 3. Mn Concentration in sediment

Location	Concentration (mg/kg, dried weight)
Station 1	13,89
Station 2	225,56
Station 3	906,74
Station 4	1.292,72
Station 5	1.626,58

The results of the analysis showed that the concentration of Mn in all stations quite diverse with the biggest concentrations was found on station 5. The concentration of Mn is high on station 5 because station 5 is located right in the confluence of the Pampang River and Tallo River, so that pollution containing Mn along the Pampang River allegedly was washed away by currents and participate accumulated around Station 5. In addition, the location of the station 5 is near the industrial and community settlement activity that triggers the high concentration of Mn. At station 1, the concentration of Mn was pretty low due on station 1 has pH 4 in the water, this makes metal Mn tend to be soluble in water compared to settles as sediment. The weather during sampling was drought so that the flow of river water heading towards the coast of Tallo River be one of the factors of how low concentration of Mn in station 1 was.

The magnitude of the concentration of Mn in sediments have been over the limit of tolerance metal Mn in sediments based on Guidelines for Classifying Sediments of the Great Lakes Harbors for Heavily Polluted by the U.S. Environmental Protection Agency i.e. 1,100 mg/kg dry weight.

2. Ferrum (Iron)

Iron waste contamination in sediments were derived from waste industrial and community activities that can be a major factor of increased Fe concentration in sediments (Dima et al., 2006). The results of the analysis of Fe in the sediments on the river Tallo were indicated on table 4.

Table 4. Fe Concentration in sediment

Location	Concentration (mg/kg, dried weight)
Station 1	356,55
Station 2	432,70
Station 3	2.650,46
Station 4	3.098,99
Station 5	2.470,17

The data in table 4 shows the concentrations of Fe in the sediments is quite large at stations 3, 4 and 5. The high concentration of Fe on the sediment was caused by the large number of industrial activity in the vicinity of airports, as well as river flow accumulative nature with a long period of time and continuously. The greatest concentration of Fe was on station 4, this is due to the location of the station 4 is located on a tributary of Pampang River which is very close to residential communities, moreover very much junk was found on station 4 while doing the sampling. While on station 1 shows the lowest concentration of Fe among the five stations because station 1 is located quite far from the residential community and industrial activity. The magnitude of Fe concentration in the sediment of the river indicates the level of Tallo impurities that is already very high. Concentrations of Fe in sediments has not exceeded the tolerance specified by the Guidelines for Classifying Sediments of the Great Lakes Harbors for Heavily Polluted by U.S Environmental Protection Agency (EPA US) which is 20.000 mg/kg dry weight

Metal Concentrations In Plant Parts

1. Manganese

Concentration of Mn in the plants give almost the same accumulation pattern in each station. At stations 1, 2 and 3 the concentration of Mn in the leaves is still very low so it is was not detected by the ICP. While on station 4 and 5, the distribution of Mn has reached the leaves which is marked by a considerable concentration of Mn in the leaves. The results of the analysis of the Mn in the Palm plant parts is shown in table 5.

Table 5. Mn Concentration in Nipah (*Nypa fruticans*) plant parts

Sample	Location	Concentration (mg/kg)
Station 1	Root	2.434,20
	Midrib	1.598,61
	Leaf	-
Total		4.032,81
Station 2	Root	2.663,28
	Midrib	1.793,90
	Leaf	-
Total		4.457,18
Station 3	Root	2.670,19
	Midrib	1.933,40
	Leaf	-
Total		4.603,59
Station 4	Root	2.997,60
	Midrib	2.002,79
	Leaf	677,55
Total		5.677,94
Station 5	Root	3.250,54
	Midrib	2.281,77
	Leaf	1.116,60
Total		6.648,91

The metal that is absorbed by plants converted into substances that are needed by the body of the plant itself. The process of changing the metals from hazardous substances into substances that are needed by the body to form a chelate is called phytochelatin. Mn that is bounded by phytochelatin will be translocated to the plant to reduce the toxicity of Mn which is accumulated on roots, in addition, translocation of Mn in plant parts also serves in the process of photosynthesis which is distributed fairly evenly every part of the plant (Buchanan et al., 2000).

2. Ferrum (Iron)

Iron analysis results in table 6 shows that concentration of Fe in the roots is more translocated to the stem, this is because Fe is an essential metal for plants which is used in the process of photosynthesis and respiration by plants. One of the factors that affect the absorption of Fe in *Nypa fruticans* plant parts is temperature. Sampling was done in dry season so the plant leaf falls to reduce evaporation, which resulted that the allocation of Fe are most numerous in the boughs. This shows that the Fe translocation in Nypa furticans is most high in the boughs.

Table 6. Fe Concentration in Nipah (*Nypa fruticans*) plant parts

Sample	**Location**	**Concentration (mg/kg)**
Station 1	Root	7.159,11
	Midrib	45.582,67
	Leaf	541,86
Total		53.283,64
Station 2	Root	7.686,18
	Midrib	46.935,42
	Leaf	305,55
Total		54.927,15
Station 3	Root	7.396,69
	Midrib	47.818,09
	Leaf	1.119,10
Total		56.333,88
Station 4	Root	39.298,56
	Midrib	49.222,80
	Leaf	38.961,42
Total		127.482,78
Station 5	Root	40.683,75
	Midrib	50.949,49
	Leaf	41.941,17
Total		133.574,41

Based on the results of the Fe analysis which is shown in Table 6, Fe accumulation is most on the stem, then the roots and leaves in a row, but the last one is a little different with 5 stations on the amount of Fe in the roots and leaves, where the leaves contain Fe more than roots, it is caused by the chosen *Nypa fruticans* plant is probably the old plants and a very little population numbers around station 5 make them slightly different from the others. Accumulated Fe has range between 600–50,000 mg/kg dry weight. This concentration is higher than the concentration of Fe in *Avicennia germinans* in Amazon River and the

Orinoco River in Brazil with 789.29 mg/kg dry weight on average (Marchand et al., 2006), even it is in contrast to the accumulation ability of *Rhizophorara cemosa* in Rivers State of Nigeria that ranges 60,79–1641,36 mg/kg dry weight (Erakhrumen, 2015).

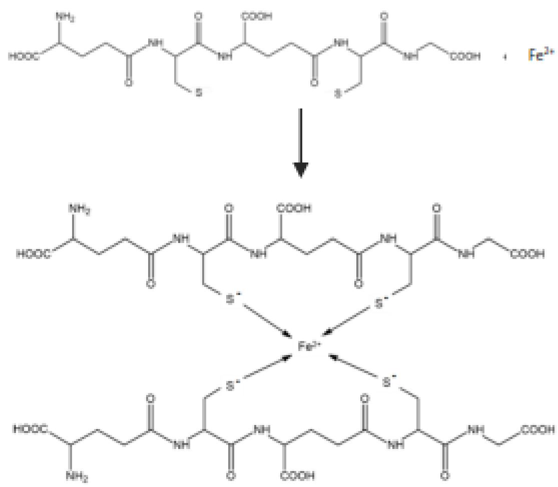

Figure 2. Phytochelatin reaction with Fe^{2+}

Physiologically metal in high concentrations will foment response to plants. According to Hirata et al (2005), the plants respond to the presence of heavy metals in the environment in various ways, one of them with a phytochelatin protein synthesis which is a specific protein synthesized herbs to detoxify heavy metals by forming complex compounds. Phytochelatins have been found in various types of plants, fungi, even up to microalgae so that compound allegedly involved in translocations of Fe in Nipah plants (*Nypa fruticans*) is phytochelatin.

Determination of Nipah Plant (*Nypa fruticans*) as Hyperaccumulator of Mn and Fe

Manganese in *Nypa furticans* plants analysis results data showed that *Nypa furticans* in Tallo River are not classified as hyperaccumulator plants of Mn. A plant is called hyperaccumulator against Mn if the ability of the plant to accumulate Mn is greater than 10,000 mg/kg dry weight. While the concentration of Fe that is accumulated in *Nypa fruticans* exceeded the minimum that is 10,000 mg/kg dry weight, so *Nypa fruticans* is said to be a hyperaccumulator against Fe (Pollard, 2009).

BCF values and TF of Mn

Data in table 7 shows the results of the calculation of the value of the BCF and TF in *Nypa fruticans* against Mn that all stations have the potential to be phytostabilization. When considered from the location of sampling, station 1, 2 and 3 is a palm plantation area, so the selected Nipah (Nypa fruticans) could be a plant that has previous harvest so the accumulation of Mn on the leaves is still low because the new Nipah grew a few months earlier, while station 4 and 5 is not a palm plantation area) so the selected nipah plants (*Nypa fruticans*) already accumulate Mn in the leaves so that sufficient concentrations of Mn were found high in leaves. Viewed from an overall BCF and TF value on table 7, it can be ensured that *Nypa fruticans* has a phytostabilization potential.

Table 7. BCF and TF values of Mn

Location	Metal Concentration (mg/kg, dried weight)				BCF	TF
	Sediment	Root	Midrib	Leaf		
Station 1	13,89	2.434,20	1.598,61	-	145,1695	
Station 2	225,56	2.663,28	1.793,90	-	9,8803	
Station 3	906,74	2.670,19	1.933,40	-	2,5385	
Station 4	1.292,72	2.997,60	2.002,79	677,55	1,4641	0,2260
Station 5	1.626,58	3.250,54	2.281,77	1.116,60	1,3626	0,3435

BCF and TF values of Fe

Data in table 8 shows that Nipah (*Nypa fruticans*), in terms of the value of TF and BCF is greater than 1, has the phytostabilization potensial. The selected *Nypa fruticans* as the object of research at station 1, 2, and 3 may be the young plants that were planted a few months back because the the sampling area is *Nypa fruticans* plantations area. But viewed from the overall value of the TF and BCF, it is certain that *Nypa fruticans* has the great phytostabilization potential when the accumulation of Fe has a minimum threshold of Fe in the sediment that is 20,000 mg/kg.

Table 8. BCF and TF values of Fe

Location	Metal Concentration (mg/kg, dried weight)				BCF	TF
	Sediment	Root	Midrib	Leaf		
Station 1	356,55	7.159,11	45.582,67	541,86	49,8141	0,0757
Station 2	432,70	7.686,18	46.935,42	305,55	42,3135	0,0398
Station 3	2.650,46	7.396,69	47.818,09	1.119,10	7,0848	0,0015
Station 4	3.098,99	39.298,56	49.222,80	38.961,42	41.1369	0,9914
Station 5	2.470,17	40.683,75	50.949,49	41.941,17	18,0250	1,0309

CONCLUSION

Based on the results of the research that has been done, then it can be concluded that the greatest accumulated Mn translocation is in the roots, while the greatest accumulated Fe translocation is on the stems. The mechanism of absorption for Mn and Fe is phytostabilization. The total of Mn accumulation in *Nypa fruticans* represents that the plant naturally does not hyperaccumulate Mn, but the total of Fe accumulation in *Nypa fruticans* suggests that this plant is naturally hyperaccumulate Fe.

REFERENCES

Anonim, 2003, *Health Effect Support Document for Manganese*, United States Environmental Protection Agency, Washington DC.

Buchanan, B., Grusen, W., dan Jones, R., 2000, *Biochemstry and Molecular Biology of Plants, American Society of Plant Physiologist*, Maryland, Amerika Serikat.

Dima, G., Popescu, I.V., Stihi, C., Oros C., Dinu S., Manea, L., dan Vlaicu, G., 2006, Fe, Mn And Zn Concentrations Determination From Ialomira River By Atomic Absorption Spectroscopy, *Romania Journal Physics*, 51(56):667-674.

Erakhrumen, A.A., 2015, Assesment of In-Situ Natural Dendroremediation Capability of Rhizophora racemosa in a Heavy MetalPolluted Mangrove Forest River State Nigeria, *Journal Application Science Environment*,19(1): 21-27.

Ghosh, M., dan Signh, S. P., 2005, Comparative Uptake and Phytoextraction Study of Soil Induced Chromium by Accumulator and High Biomass Weed Species, *Applied Ecology and Environmental Research*, 3(2): 67-79.

Hirata, K., Tsuji, N., and Miyamoto, K., 2005,Biosynthetic Regulation of Phytochelatins,Heavy Metal-Binding Peptides, *Journal of Science and Bioengineering*, 100(6): 593-599.

Juhaeti, T., Syarif, F., and Hidayati, N., 2004, Inventory of Potential Plants for Fitoremediation of Land and Degraded Water in Gold Mining, *Biodiversity*, 6 (1): 31-33.

Kariada, N.T.M., and Irsadi, A., 2014, Role of Mangroves as Biofilter of Water Pollution in Semarang Treadfish Pond Area, *Human Journal and Environment*, 21 (2): 188194.

Liong, S., Noor, A., Taba, P., and Abdullah A., 2010, *Phytoaccumulation of Pb Study in Kankung Darat (Ipomoea reptans Poir)*, Department of Chemistry, Faculty of Mathematics and Natural Sciences, Hasanuddin University, Makassar..

Pollard, A., J., 2009, Manganese Hyperaccumulation in Phytolacca americana L.from the Southeastern United States,*Northeastern Naturalist*, 16(5): 155-162.

Setiawan, H., 2014, Pollution of Heavy Metals in the Coastal Waters of Makassar City and their Mitigation Efforts, *EBONI Technical Info*, 11 (1): 1-13.

Widowati, W., Sastiono, H., and Jusuf, R., 2008, *Effects of Toxic Metals on Pollution Prevention and Control*, Andi, Yogyakarta.

Yudo, S., 2006, Pollution Conditions of Heavy Metal in DKI Jakarta River Waters, *JAI*, 2 (1): 1-15.