

The Fitoremediation of Pb and Zn in the Siak River By *Ceratophyllum demersum*

Budijono¹, Muhammad Hasbi², Eko Purwanto³, Kamaruddin Eddiwan⁴, Bethani YunitaSinaga⁵

Faculty of Fisheries and Marine, University of Riau, Binawidya Campus, Jln HR Soebrantas KM 12.5, Charming, Pekanbaru City, Riau, Indonesia

Abstract: *Ceratophyllum demersum* is a type of drowning macrofoam commonly used in heavy metal phytoremediation in water. This study focused on assessing the ability of *C. demersum* to accumulate heavy metals (Pb and Zn) into their body tissues from heavy metals contained in the water of the Siak River. This plant is grown in a natural condition (S. Siak) at different water depth (0;0,5;1 m) with aquatic plant floating raft. Water measurements and water sampling as well as entire plant tissue per depth for calculated heavy metals at different time intervals (6, 12, 18, 24, 30 days). The results show that the Siak River has been contaminated with Pb and Zn and the concentration of Pb > Zn in *C. demersum* with each Pb from 0 - 1m water depth is 12.641 mg/kg, 15.659 mg/kg and 16.604 mg/kg of the initial concentration of 0.158 mg/kg. The average absorption rate and Pb accumulation per depth are 78.86%, 97.92% and 103.89%, respectively. It was concluded that phytoremediation of heavy metal Pb in Siak River was effective with *C. demersum* up to a water depth of 1 m.

Keywords: Phytoremediation, Heavy Metal, *Ceratophyllum demersum*, Siak River

1. Introduction

Siak River is one of the 4 largest rivers within the authority of Riau Province with a length of \pm 300 km, a width of 100-150 m and a depth of 15-25 m across 5 districts (Bengkalis, Kampar, Rokan Hulu, Siak and Pekanbaru). Along the banks of this river has been used for various activities, including plantation, settlement, industry (palm oil, plywood, chemical, pulp and paper, chemical), fishery, market, port, shops, water transport and mining excavation C and others. These activities produce liquid waste, directly and indirectly, contain a variety of compounds in it, so that now there is a decrease in water quality and threaten the sustainability of aquatic biota in it. Monitoring results on 17 monitoring points from upstream to downstream of the Siak River show heavily polluted status (BLH Riau Province, 2010, 2013 and 2015). Among other pollutants are heavy metal, which is cumulative and carcinogenic and difficult to lose in water because heavy metals can not biodegradable. Heavy metals tend to form organic alliances of organic compounds (Sumarjo, 2009).

Pb and Zn are the 2 highest heavy metals in Siak River, especially in Pekanbaru City area with Pb range 0,024 - 0,059 mg / L and Zn 0,016 - 0,058 mg / L (BLH Riau Province, 2015). The impact caused by heavy metals for aquatic organisms is the disruption of body metabolism due to obstruction of enzyme work in physiological processes. Pb and Zn can accumulate in the body and are chronic which eventually result in the death of aquatic biota (Palar, 2008).

Phytoremediation is an exciting and much-reviewed effort to recover or clean heavy metals in water using aquatic plants. Aquatic plants sinks play a key role in the shallow freshwater ecosystem. They provide habitat and protection for predatory fish and zooplankton, which can indirectly inhibit the abundance of phytoplankton (Jepessen et al., 1998) with competition for nutrients and allelopathic activity (Scheffer et al., 1993; Nakai et al., 1999). Macrophytics reduces the resuspension process and increases the

sedimentation rate, which increases water transparency (Madsen et al., 2001; Søndergaard et al., 2003).

Ceratophyllum demersum as a drowning aquatic plant has been widely tested as a phytoremediator agent against heavy metals common to controlled conditions (laboratory) by various outside and domestic researchers. However, testing of more complex and dynamic river environments affecting the ability of these plants to accumulate heavy metals is still very low. Therefore, this study aims to assess the ability of *C. demersum* in accumulating heavy metals of Pb and Zn in flowing waters, ie Siak River.

2. Method

This research was conducted in May - September 2017 at Siak River, Pekanbaru City, Riau Province. Analysis of heavy metals (Pb and Zn) and TSS at the Riau Riau University's FPK Fibers Integrated Laboratory. The materials used are Siak River samples, *C. demersum* crops, HNO₃, 1500 ml used plastic bottles, nylon plastic bag straps, label paper, markers, and stationery. Among the tools used are analytical scales 0.0001 g, pH meters, current draught, coolbox, stopwatch, mercury thermometer, AAS Perkin-Elmer brand and Secchi disk.

C. demersum plants were floated with two floating raft units. A rectangular square-shaped raft of 5 m (P) x 2.5 m (L) with a 1500 mL bottle of the water bottle on each side of the map. Inside the floating raft is divided into 10 plots with a size of 1 x 1 m² so obtained 2 rows of *C. demersum* plot. In each of the plots are given nylon ropes with a distance of 25 cm on each side of the length and width of the plot that serves to hang the aquatic plants. In each plot, there are 4 ropes suspended into the water with a length of 1.5 m which is given a weight. Each rope has tied the plant to the water depth strata that is: 0 m (the water surface); 0.5 m and 1 m. Plants attached to each rope in each plot of 50 g have been acclimatized. This plant is collected from a pool of water in the environment of the University of Riau as much as 5 kg

by hand collecting, then washed and put into a tarpaulin pond for ± 1.5 months with the turn every 3 days. A week before use, 50 g of plants (leaves and stems) was taken randomly from the tarpaulin pond for known early heavy metals.

Subsequent crop sampling was carried out at each water depth with a time of 6, 12, 18, 24 and 30 days at 50 g randomly on each rope in the plot, then inserted into a plastic bag separately and labeled according to the depth of water planted for the plant dried in the oven at 60 - 70 oC for 2 days and taken 1 g for the destruction process and continued heavy metal analysis of Pb and Zn using Perkin Elmer AAS at a wavelength of 217 nm for metal Pb and at a wavelength of 213.9 nm for metal Zn.

Water quality data including temperature, brightness, current velocity, pH, DO, TSS and heavy metals (Pb and Zn) in water and *C. demersum* are presented in table and graph form and then discussed descriptively qualitatively. Water quality data compared to water quality standard (PP.82 / 2001), except the brightness and current velocity.

3. Results

Water quality and heavy metals (Pb and Zn)

The quality of the Siak River water obtained shows the brightness range of 20.5 - 37 cm, current velocity of 11 - 13 cm / s, temperature 26 - 29 oC, pH 5.19 - 6.39, TSS 34 - 60 mg / L, DO 4.01 - 4.19 mg / L, Pb 0.2110 - 0.7870 mg / L and Zn 0.1320 - 0.2785 mg / L. The mean concentration of Pb 0.5426 mg / L is higher than Zn 0.2145 mg / L.

Absorption and Accumulation of Heavy Metals at *C. demersum*

Before use, *C. demersum* has a concentration of Zn (14,513 mg / kg) > Pb (0.158 mg / kg). After a month planted into the water at a water depth stratum (0; 0.5; 1 m) experienced an average increase in concentration sequentially for Zn to 15.837 mg / kg, 16.337 mg / kg and 21.417 mg / kg. Similar conditions also apply to Pb to 12.641 mg / kg, 15.659 mg / kg and 16.604 mg / kg (Fig. 1).

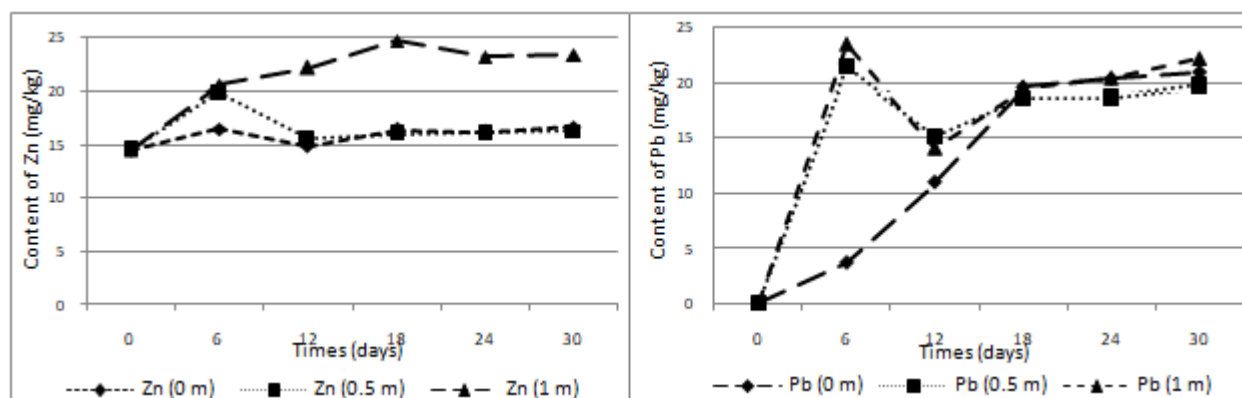


Figure 1: Content of Zn and Pb in Plant *C. demersum*

The absorption and accumulation of heavy metal Pb by *C. demersum* on the surface of water (0 m) increased linearly in line with the observation time of 23.36% (day 6) to 124.03% (30th day), while at strata 0.5 and 1 m highest on the 6th day in sequence, ie 134.30% and 146.71%. In contrast, the rate of accumulation of this plant to Zn is much lower (<1%)

with the highest accumulation rate and continues to increase over time, especially in the water depth stages of 1 m compared to strata 0 - 0.5 m which is only the highest achieved on day 6 and decreased to the end of the study (Figure 2).

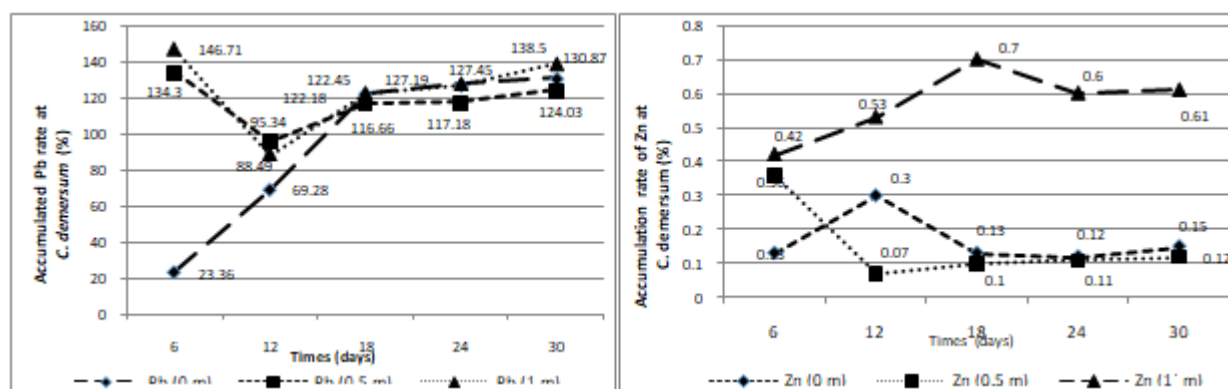


Figure 2: Accumulation Rate and Accumulation of Pb and Zn by Crop *C. demersum*

4. Discussion

The Siak River water transparency is low because it is influenced by peat water with blackish brown and suspended

particles above the water quality standard, but can still support the life of *C. demersum* planted beyond this measured water-brightness limits. Current velocity during research is low because it is not influenced by rain

conditions that can increase the flow of river water. Water temperatures are within the normal range for aquatic biota life, including these plants, even these plants are able to live within the 10-19 ° C (Al-Ubaidy and Rasheed, 2015) and 27-34°C (Suryadi, Apriani and Kadaria, 2016) range. The plant is able to grow in acidic (low pH) water environments that differ from the results of Al-Ubaidy and Rasheed's research (2015) with a pH range of 7-7.3. In water, concentrations of heavy metals $Pb > Zn$ and both have exceeded the water quality standard (PP.82 / 2001), ie Pb 0.03 mg / L and Zn 0.05 mg / L.

The tested plant is able to absorb nutrients in water so that it can survive on polluted media of Pb and Zn . This is because it has several major mechanisms for dealing with heavy metal stresses such as *Elodia Canadensis*: (1) mitigation (amelioration), the plant absorbs the ion, but acts in such a way as to minimize its influence by including chelating formation, dilution, localization or even excretion; and (2) tolerance, plants can develop metabolic systems that can function at potentially toxic concentrations with enzyme molecules (Fitter & Hay, 1992 in Novita, Yuliani and Purnomo, 2012).

From the research conducted, the results obtained that absorption and accumulation of heavy metals Pb and Zn by *C. demersum* from initial concentration. The concentration of $Zn > Pb$ is influenced by high starting Zn in this plant. Absorption and accumulation of the largest Zn in strata 1 m from day 0-18 and tend to be stable until day 30 compared to strata 0 m and 0.5 m. This is related to the role of Zn as the heavy metal essential for *C. demersum* growth so that more accumulated Zn can increase chlorophyll formation for the photosynthesis process, although the light intensity at 1 m depth is very low due to the brightness of Siak River water reaching only 37 cm. In contrast, the absorption and accumulation of Pb by this plant are actually the largest compared to Zn in terms of initial concentrations of Pb in plants. In the 0.5 m and 1 m strata, the largest absorption and Pb accumulation were achieved on day 6 and tended to increase with time in the same water-splitting conditions. This increasing concentration of Pb is due to Pb instead of the essential heavy metals. According to Kabata-Pendias & Pendias (1984 in Saygideger et al., 2004), lead metal (Pb) has not proven important in plant metabolism, although it occurs naturally in all plants.

Based on absorption and accumulation of Zn which persists until day 30 and highest in the 1 m strata indicates the presence of Pb both in water and in this plant may have a small effect on the process of photosynthesis, the availability of nutrients in water and the uptake of nutrients to the plant this requires further observation. This is due to the presence of lead (Pb) taking part in the disruption of the photosynthesis process due to the disruption of enzymes that contribute to the biosynthesis of chlorophyll aminolevulinic acid (ALAD) catalyzes the formation of porphobilinogen (Singh 1995 in Saygideger et al. 2004), resulting in excess metal Pb in plants have an effect on the inhibition of chlorophyll biosynthesis (Miranda and Ilangovan, 1996 in Saygideger et al., 2004). Heavy metal Pb is reported to disrupt the granular structure of chloroplasts (Mishra & Dubey, 2005a). The formation of chloroplast structure is

influenced by mineral nutrients such as Mg and Fe . Excessive heavy metal entry in plants such as Pb will reduce Mg and Fe intake, causing changes in volume and number of chloroplasts (Kovacs, 1992 in Sembiring and Sulistyawati, 2006). According to Mishra and Dubey (2005b), Pb on excessive planting media can lead to the limited amount of nutrients needed in plant tissues that cause the development and growth of water plants to decline. The cationic nutrients such as K^+ , Ca^{2+} , Mg^{2+} , Mn^{2+} , Zn^{2+} , Cu^{2+} , and Fe^{3+} , and the NO_3 anions are inhibited to the plant root by Pb .

In general, the absorption and accumulation of both heavy metals by these plants are quite high in the waters of the Siak River which has a low water level and low pH and the colour of blackish brown water. The results of Pb uptake and accumulation by *C. demersum* from this study were higher than those in the same plant capable of absorbing Pb of 10.7 mg/kg or 9.3 mg/kg in *Potamogeton natans* and lower in *Elodea canadensis* which reached 27.4 mg/kg by Osmolovskaya and Kurilenko (2005). The absorption rate and accumulation of these relatively high metals are influenced by low pH. This refers to the highest accumulation of As by *C. demersum* at pH 5 and decreases if the pH value increases (Khang, Hatayama and Inoue, 2012). In environments that contain heavily plant-heavy metals make regulatory proteins and these plants hold gene expression to form a binding compound called phytochelatin. Phytochelatin is a peptide containing 2-8 kinds of amino system in the centre of the molecule as well as a glutamate acid and a glycine at opposite ends. Fitokhelatin is formed in the nucleus which then passes through the endoplasm (RE), the Golgi apparatus, the secretory vascula to reach the cell surface. This phytochelatin contains many SH^- , S^+ , and RS^- groups. This functional group is present in the amino acid system which is a phytochelatin builder compound. Phytochelatin will form sulphide bonds at the tip of sulfur in cysteine when encountered with heavy metals and form complex compounds so that heavy metals will be transported to plant tissues (Salisbury & Ross 1995 in Novita et al., 2012). The absorption and accumulation of both heavy metals by *C. demersum* through the entire surface of the body (stems and leaves), because it has very thin cuticles that facilitate the removal of metal from water (Prasad, 2008). The process of absorption of heavy metals by aquatic plants is largely a passive process, which in this process does not require ATP but a small part involved in cellular metabolism (Connel and Miller, 1995 in Novita et al., 2012).

The absorption and accumulation of both metals in this plant do not decrease the two metals in the Siak River as planting medium because it is carried out directly in natural flowing waters that continuously receive these metal inputs from various sources of non-point sources. Even similar conditions are also found in laboratory studies of absorption of Pb by *Elodea canadensis* which is not proportional to the decrease in Pb on planting medium by Novita et al. (2012), caused by heavy metals that have entered the plant body will be excreted by aborting the old leaves so as to reduce the concentration of metal Pb (Priyanto, 2008 in Novita et al., 2012) or due to the precipitation of Pb in the form of salt molecules in water if the pH of the media is alkaline (Darmono, 1995).

5. Conclusion

Based on this research can be summarized as follows: (1) Siak River has experienced heavy metal pollution Pb and Zn; (2) there is a difference of concentration of heavy metals (Pb and Zn) in *C. demersum* based on different water depth strata with highest Zn concentration over time in the 1 m strata and highest Pb in strata 0.5 m and 1 m; and (3) there is a difference in the absorption and accumulation of heavy metals (Pb and Zn) by *C. demersum* based on different water depth strata with highest absorption of Pb over time in strata 0.5 and 1 m

References

- [1] Al-Ubaidy, H.J. and K.A. Rasheed. 2015. Phytoremediation of Cadmium in river water by *Ceratophyllum demersum*. World J Exp Biosci, 3: 14-17.
- [2] Connel, D.W. dan G.J. Miller. 1995. Kimia dan Ekotoksikologi Pencemaran. UI Press, Jakarta.
- [3] Darmono. 1995. Metal in Biological Systems of Living Beings. UI Press, Bogor.
- [4] Environment Agency of Riau Province. 2010. Water Quality Monitoring Report for Siak River Year 2010. BLH Riau Province, Pekanbaru.
- [5] Environment Agency of Riau Province. 2013. Water Quality Monitoring Report for Siak River Year 2013. BLH Riau Province, Pekanbaru.
- [6] Environment Agency of Riau Province. 2014. Kampar River Water Quality Monitoring Report 2014. BLH Riau Province, Pekanbaru.
- [7] Environment Agency of Riau Province. 2015. Water Quality Monitoring Report for Siak River Year 2015. BLH Riau Province, Pekanbaru.
- [8] Khang, H.V., M. Hatayama dan C. Inoue. 2012. Arsenic accumulation by aquatic macrophyte coontail (*Ceratophyllum demersum* L.) exposed to arsenite and the effect of iron on the uptake of arsenite and arsenate. Environmental and Experimental Botany, 83: 47-52.
- [9] Madsen, J.D., P.A. Chambers, W.F. James, E.W. Koch and D.F. Westlake. 2001. The interaction between water movement, sediment dynamics and submerged macrophytes. Hydrobiologia, 444: 71-84.
- [10] Mishra, S and R.S. Dubey. 2005a. Heavy Metal Toxicity Induced Alterations in Photosynthetic Metabolism in Plants. India: Banaras Hindu University. Accessed in [http://www.psi.cz/ftp/ola/Handbook%20of%20Photosynthesis / DK3138ch44. pdf](http://www.psi.cz/ftp/ola/Handbook%20of%20Photosynthesis%20DK3138ch44.pdf). on September 23, 2016.
- [11] Mishra, S and R.S. Dubey. 2005b. Toxic Metal on Plants. India: Banaras Hindu University. Accessed in <http://www.scielo.br/..a04v17n1.pdf>. On January 15, 2012.
- [12] Nakai, S., I. Inoue, M. Hosomi, and A. Murakami. 1999. Growth inhibition of blue-green algae by allelopathic effects of macrophytes. Water Sci. Technol. 39: 47-53.
- [13] Novita, Yuliani and T. Purnomo, 2012. Absorption of Lead Metals (Pb) and Chlorophyll Elodea canadensis on Liquid Wastes of Pulp and Paper Lanterns Bio, 1 (1): 1-8.
- [14] Osmolovskaya, N. and Kurilenko, V. 2005. Macrophytes in phytoremediation of heavy metal contaminated water and sediments in urban inland ponds, Geophysical Research Abstracts, (Online), Vol. 7. accessed in [HTTP: //meetings.copernicus. org / www / cosis.net / abstracts / EGU05-J-10510.pdf](http://meetings.copernicus.org/www/cosis.net/abstracts/EGU05-J-10510.pdf). On April 19, 2011.
- [15] Palar, H. 2008. Heavy Metal Pollution and Toxicology. Rineka Cipta, Jakarta.
- [16] Prasad, M.N.V. 2008. Aquatic Plants for Phytotechnology. Diakses Dalam <http://sumarsih07.files.wordpress.com/2008/09/aquatic-plant.pdf>. Pada Tanggal 26 January 2015.
- [17] Riau Environmental Impact Management Agency. 2005. Siak Watershed Conservation Study 2005. Bapedal Riau Province, Pekanbaru.
- [18] Saygideger, S., D. Muhittin, dan K. Gonca. 2004. Effect of Lead and pH on Lead Uptake, Chlorophyll and Nitrogen Content of Typha latifolia L. and *Ceratophyllum demersum* L. International Journal of Agriculture and Biology. Diakses dalam http://www.fspublishers.org/ijab/past-issue/IJABVOL_6_NO_1/39.pdf. Pada Tanggal 13 Maret 2017.
- [19] Scheffer, M., S.H. Hosper, M.L. Meijer, B. Moss and E. Jeppesen. 1993. Alternative equilibria in shallow lakes. Trends Ecol. Evol. 8: 275-279.
- [20] Sembiring, E. and E. Sulistyawati. 2006. Accumulation of Pb and its effect on leaf condition of Swieteniamacrophylla King. Research School of Life Sciences and Technology (SITH), Bandung Institute of Technology. Accessed in http://www.sith.itb.ac.id/profile/databuendah/Publications/7.%20Ebinthalina_IATPI2006.pdf. On March 13, 2016.
- [21] Søndergaard, M., J.P. Jensen and E. Jeppesen. 2003. Role of sediment and internal loading of phosphorus in shallow lakes. Hydrobiologia, 506-509: 135-145.
- [22] Sumardjo, D. 2009. Introduction to Chemistry. EGC Medical Book Publishers, Jakarta.
- [23] Suryadi, I. Apriani and U. Kadaria. 2016. Coontail Plant Test (*Ceratophyllum demersum*) As Phytoremediation Agent of Liquid Coffee Waste. Department of Environmental Engineering Department of Civil Engineering Faculty of Engineering University of TanjungPura, Pontianak. <https://media.neliti.com/media/publications/191710-ID-none.pdf>. Retrieved 16 November 2017. At 10:15 pm.