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PHYTOREMEDIATION DYNAMIC MODEL OF HEAVY METAL MERCURY (Hg) IN MANGROVE *(Avicennia alba)* AT WONOREJO RIVER ESTUARY

Anis Zusrin Qonita*, Harmin Sulistiyaning Titah and Uridna Marwah Luthtansa

Department of Environmental Engineering, Faculty of Civil, Planning and Geo Engineering, Institut Teknologi Sepuluh Nopember, Keputih, Sukolilo, 60111 Surabaya, Indonesia

*Corresponding Author: aniszusrinqonita@gmail.com

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Abstract

Industrial and domestic activities resulted in heavy metal contamination of heavy metals mercury (Hg) in the river that flows towards the coast of Surabaya, Indonesia. One of the pollution control efforts is phytoremediation. Phytoremediation has the advantage that it is cheaper and easier to implement. The plant used in this phytoremediation process is *Avicennia alba* because it can absorb and accumulate heavy metals mercury (Hg). This research was conducted at the Wonorejo Mangrove Ecoforest. Samples were taken in the form of water, sediment, roots, stems and leaves of *Avicennia alba* and analyzed for Hg concentration using atomic absorption spectrophotometry (AAS). The results showed that the average metal Hg in sediment at station A was 0.026 mg/kg, station B was 0.038 mg/kg and station C was 0.0003 mg/kg. The concentration of Hg in Wonorejo waters has a value range of <0.0003 mg/L to 0.099 mg/L. The average bioconcentration factor (BCF) value of mangrove *Avicennia alba* is 47.31. Meanwhile, *Avicennia alba*'s translocation factor (TF) value in absorbing heavy metal Hg showed more than 1 and less than 1. This indicates that *Avicennia alba* carries out an extraction and translocation process. Based on the results of the dynamic system, there is a mutually influencing relationship between sediment, BCF and TF. The highest translocation ability occurs in the stem, so it can be concluded that *Avicennia alba* has the potential to absorb heavy metal Hg in the coastal area of Surabaya.

INTRODUCTION

The estuary of the Wonorejo River is located on the east coast of Surabaya, Indonesia, which is the meeting point of the watershed and the coastal area. The water found at the mouth of the Wonorejo river comes from the Jagir and Brantas rivers. The trajectory of the Brantas and Jagir streams with paths passing through residential and industrial areas makes the river tend to change its function into a dumping ground for domestic and industrial waste [1]. The number of industries in the city of Surabaya has increased every year. In 2019, large and medium industries in the city of Surabaya reached 31,695 industries, while in 2015 only reached 957 industries [2]. The emergence of the high number of these industries also causes various environmental problems, such as water, air and soil pollution. The same thing happened in the rivers of Surabaya City. According to [3], Heavy metal pollution in the rivers of Surabaya city has increased. Heavy metals such as mercury (Hg), cadmium (Cd), Lead (Pb) and Zinc (Zn). These heavy metals generally come from anthropogenic activities, namely industrial, fuel, household (domestic), and agricultural [4].

According to Gina (2013), researching heavy metals around the coast of Surabaya has found that the total mercury content in the gills of mussels ranges from 0.593-1.892 ppm. In meat, it ranges from 0.198-0.758 ppm, in the stomach, the mercury content ranges from 0.987-2.904 ppm and in the shells ranges from 0.379-1.118 ppm. The mercury (Hg) content in the green mussels has exceeded the allowable limit. The maximum limit of mercury (Hg) content in the body of fish consumed by humans, according to FAO/WHO in Gina (2013), is 0.05 ppm. In addition, the concentration of heavy metal mercury (Hg) on the east coast of Surabaya was obtained at 0.015-0.017 ppm with an average value of 0.016±0.001 ppm. The concentration is classified as high according to the seawater quality standards in the Decree of the Minister of the Environment Number 51 of 2004 Appendix 3 concerning Sea Water Quality Standards for Marine Biota, which is 0.001 ppm [6].

One of the efforts that can be done to reduce and control the presence of heavy metal mercury pollution is the phytoremediation process. Control efforts with environmental rehabilitation methods are generally costly. Therefore, phytoremediation is an alternative method of controlling heavy metals that is cheap and easy to implement. There are several types of phytoremediation: phytoextraction, rhizofiltration, phytodegradation, phytostabilization, and phytovolatilization. [7]. In the phytoextraction process, roots take contaminants and translocate them to roots, leaves, or plant stems. The process is often used to remediate heavy metals such as Ag, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb and Zn. Plants that are often used in the phytoremediation of heavy metals include mangroves, *Azolla pinnata*, *Thlaspi caerulescens*, *T. calaminere*, *Jatropha curcas* [8][9][10].

Dynamic system is an approach to solving a problem in a complex system. Solving these problems will be in the form of alternative policy scenarios. The advantage of a dynamic system is that it is an approach that can identify real things by paying attention to the complex components [11]. Dynamic systems are much better at long-term, medium-term, or short-term predictions [12].

This study aims to determine the dynamics of the phytoremediation system of *Avicennia alba* mangroves at the Wonorejo River estuary in accumulating heavy metal mercury (Hg) by determining the value of the bioconcentration factor (BCF) and the value of the translocation factor (TF).

MATERIALS AND METHODS

Sampling Location

The research was conducted in a mangrove forest at the estuary of the Wonorejo River. Sampling was carried out at three stations, namely station A, station B and station C. Station A is a station directly adjacent to the river estuary which acts as the initial point of entry of pollutants into the sea, station B is a station in the middle between stations A and C, while station C is the station with the farthest location from the pollutant source and directly with the sea (Figure 1). The selection of the sampling location was based on the thickness of the mangrove forest, which was seen visually through Google earth, the distance between the mangrove forest and the pollutant source and the safety factor. The method used in sampling is the quadrat transect method (**Figure 2)**. The transect plot used is a checkered transect line. The transect line is perpendicular to the coastline towards the land (mangrove forest). The length of the transect line used for the forest is 30 meters. The plot sizes under the transect method are 10m x 10m for trees/poles, 5m x 5m for saplings, and 2m x 2m for seedlings. In this study, the plot size used was 10m x 10m for trees/poles because the samples taken were trees with tree diameters of more than 10 cm. In this study, there are seven sampling points. Coordinates of sampling points can be seen in **Table 1.**

Figure 1. Sampling Location.

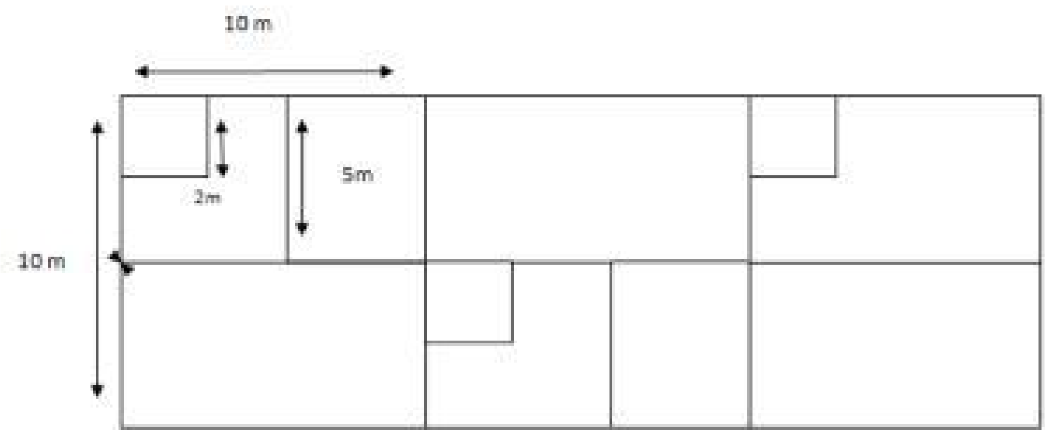

Figure 2. Transek Method.

Table 1. Coordinate sampling point.

Point	Coordinate
SAP1	SS 7°18'19.75" E 112°50'39,4"
SAP2	SS 7°18'20.21" E 112°50'39.05"
SAP3	SS 7°18'20.56" E 112°50'38.23"
SBP1	SS 7°18'20.19" E 112°50'40."
SBP2	SS 7°18'20.39" E 112°50'39.92"
SBP3	SS 7°18'20.53" E 112°50'39.64"
SCP3	SS 7°18'21.98" E 112°50'39.52"

Parameter Analysis

In this study, atomic absorption spectrophotometer (AAS) SNI 06-6992.2-2004 and US EPA SW-846-3050 B & 7420 were used to analyze heavy metal mercury (Hg) in sediments, roots, stems and leaves. Meanwhile, the pH parameter was measured using a pH meter, the temperature was measured using a thermometer and salinity was measured using a refractometer.

Determine of Bioconcentration Factor (BCF) and Translocation Factor (TF)

The ability of plants to remove pollutant compounds from contaminated soil media can be seen from the value of the Bioconcentration Factor (BCF). BCF is the ratio of the concentration of heavy metals in plant tissues (roots and leaves) with the concentration of the adjacent environment. While the Translocation Factor shows the transfer of heavy metals from roots to leaves, stems and leaves. BCF and TF can be used as indicators to see the ability of plants in the process of phytoremediation [13]. Determination of BCF and TF values can be seen in the following equations [14]:

$$\mathrm{BCF} = \frac{[\mathrm{Hg}_{\ \mathrm{root}}]}{[\mathrm{Hg}_{\ \mathrm{media}}]} \tag{1}$$

$$TF\ root - shoot = \frac{[Hg\ \ shoot]}{[Hg\ in\ root]} \tag{2}$$

$$TF\ shoot - leaves = \frac{[Hg\ in\ leaves]}{[Hg\ in\ root]} \tag{3}$$

$$TF\ root - leaves = \frac{[Hg\ in\ leaves]}{[Hg\ in\ root]} \tag{4}$$

The results of the BCF were categorized in the BCF classification to determine the type of accumulator plant (**Table 2).**

Table 2. Category of BCF.

Category	Range
High accumulator plants	1-10
Moderate accumulator plants	0.1 – 1
Low accumulator plants	0.01 – 0.1
Non accumulator plants	< 0.01

Dynamic System

Dynamic systems emerge as solutions to complex problems due to cause and effect [15]. The principle of dynamic systems is that the model represented must match or approach real life. In the process, the data used in the dynamics analysis of the system uses real data that occurs in the field. [16]. The stages of dynamic system modeling, according to Muhammadi et al. (2001) in Subiantoro [17], among others,

1. Concept of generation

The first stage in making a dynamic system model is recognizing the problem, looking for actors to handle the problem and the causes. Next, create a mental pattern or model described in the Causal Loop Diagram (CLD).

2. Modeling

After the CLD is formed, a Stock Flow Diagram (SFD) is created using software that uses symbols. The symbols are stock (level), flow (rate), auxiliary and constant.

3. Inputting Data

Primary data or secondary data that have been obtained are entered into the model as stock, flow, auxiliary and can also be constant.

4. Model simulation

First, the timing, integration method, and time stages are determined to obtain a graph of the behavior of time.

5. Model validation

Checked and evaluated the model following applicable principles.

RESULTS AND DISCUSSIONS

Based on the research results, it is known that the highest concentration of mercury (Hg) in sediment is at the sampling point of SBP1 which is 0.069 mg/kg and the concentration of mercury in water is at the sampling point of SCP3 which is 0.099 mg/L. While the highest concentrations in roots, stems and leaves were 0.099 mg/kg, 0.11 mg/kg, 0.015 mg/kg, respectively.

The concentration of Hg in the sediment at all sampling locations can be seen in Fig 3. The Hg concentrations were 0.029 mg/kg, 0.03 mg/kg, 0.019 mg/kg, 0.069 mg/kg, 0.049 mg/kg, 0.005 mg/kg, 0.0003 mg/kg **Figure 3**.

The average concentration of Hg in the sediment at station A was 0.026 mg/kg, station B was 0.038 mg/kg and station C was 0.0003 mg/kg. The highest average Hg concentration was at stations A and B, while the lowest was at station C. The Hg concentration in sediment at the Wonorejo River estuary ranged from <0.0003 to 0.038 mg/kg. Based on this, it can be seen that the concentration of Hg at the three stations decreased with increasing distance from the station location to the river mouth. The contours of the area can influence the Hg concentration. The distribution contours of Hg metal in the sediments of the Wonorejo River estuary can be seen in **Figure 4**. The concentration of dissolved Hg^{2+} was found at the bottom of the water column due to the nature of Hg, which easily settles in the sediment in the form of particulates.

The distribution of Hg metal in the three stations shows that the closer to the river mouth, the higher the concentration and the further away from the river mouth, the lower the concentration. The highest concentration of Hg is near the river mouth, which is directly opposite the sea. The high concentration of Hg metal near the river mouth can be caused by heavy metals, which have a high density and quickly accumulate in sediments. [17].

Figure 5 shows the concentration of Hg in water at all sampling locations. Concentration of Hg in water at all sample points were 0.0003 mg/L, 0.015 mg/L, 0.01 mg/L, 0.005 mg/L, 0.0003 mg/L, 0.0003 mg/L, 0.099 mg /L. The concentration of Hg in Wonorejo waters has a value range of <0.0003 mg/L to 0.099 mg/L. The highest average concentration of Hg is found in the waters of station C. This is because at station C the concentration of Hg is influenced by salinity. The salinity at station C is the highest compared to stations A and B. The location of station C has high salinity because it is directly adjacent to the sea. High salinity will cause heavy metal content in the waters to be high, and vice versa, low salinity causes heavy metals in the waters to be low [18].

Figure 6 illustrates the BCF value calculated based on equation 1. Based on the figure, the BCF value of *Avicennia alba* on Hg is 0.01; 0.5; 0.52; 0.073; 0.006; 0.06; 330. The average BCF value of mangrove *Avicennia alba* is 47.31. This shows that *Avicennia alba* is a plant accumulator to hyperaccumulator of heavy metal Hg based on the **Table 3**.

Meanwhile, the TF value of *Avicennia alba* in absorbing heavy metal Hg showed more than one and less than 1. Based on this, it can be concluded that *Avicennia alba* mangrove plant is a Hg accumulator plant. The table is the TF value calculated based on equations 2, 3 and 4.

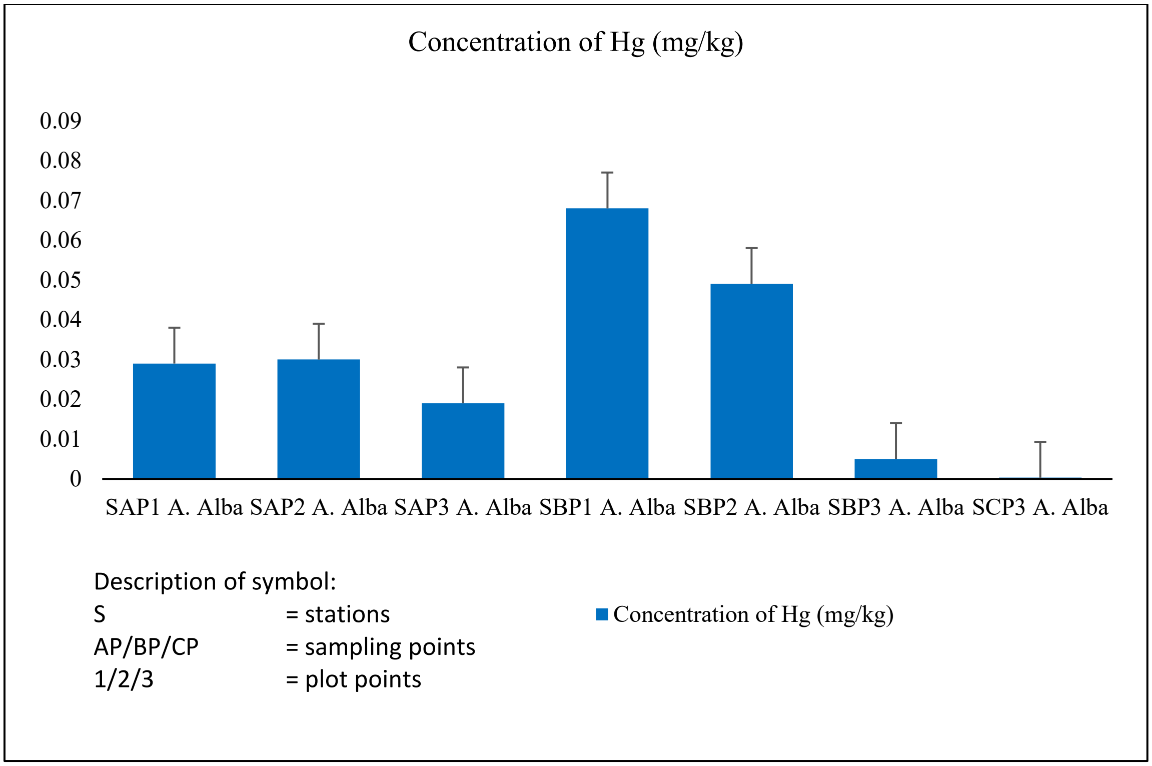

Figure 3. Concentration sediment of Hg in all location sampling.

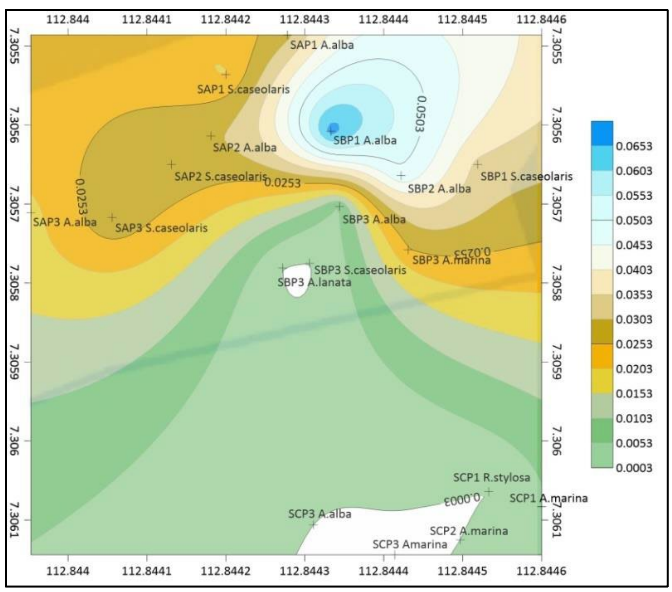

Figure 4. Distribution contour Wonorejo River estuary.

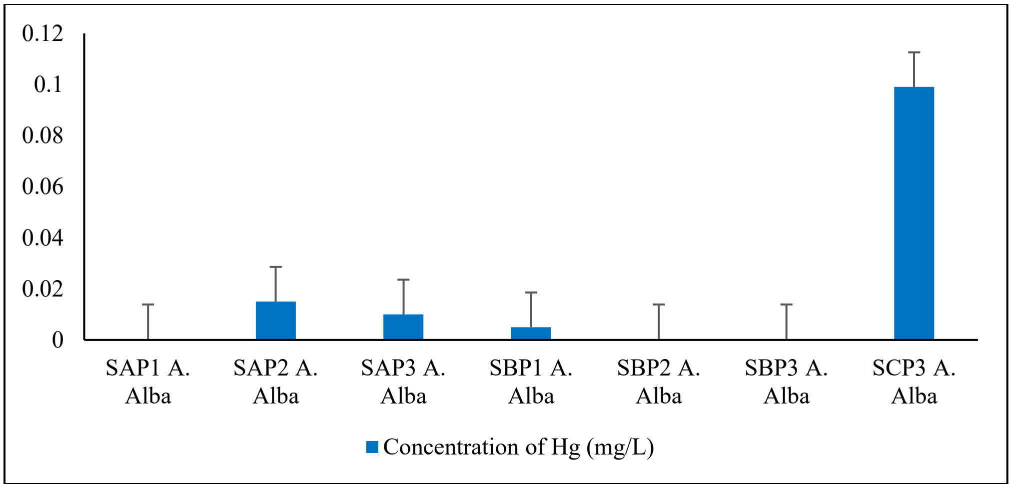

Figure 5. The concentration of Hg in water at all points of sampling locations.

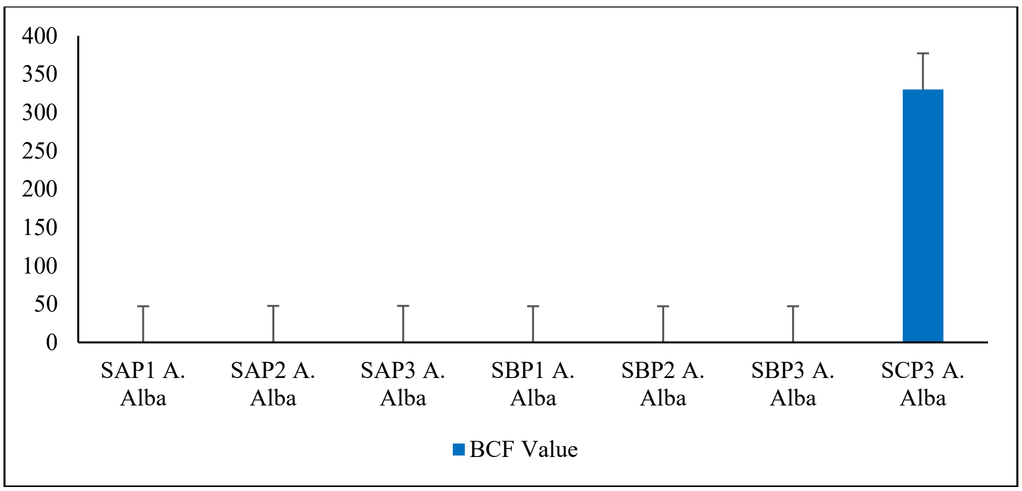

Figure 6. BCF value of *Avicennia alba* on Hg.

Table 3. TF value of *Avicennia alba* on Hg.

Point	Concentration Hg on Roots (mg/kg)	Concentration Hg on Steems (mg/kg)	Concentration Hg on Leaves (mg/kg)	TF Roots-Steems	TF Steems-Leaves	TF Roots-Leaves
SAP1 *A. Alba*	0.0003	0.0840	0.0003	280.00	1.00	1.00
SAP2 *A. Alba*	0.0150	0.0640	0.0003	4.27	0.02	0.02
SAP3 *A. Alba*	0.0100	0.0590	0.0050	5.90	0.50	0.50
SBP1 *A. Alba*	0.0050	0.0520	0.0003	10.40	0.06	0.06
SBP2 *A. Alba*	0.0003	0.0440	0.0050	146.67	16.67	16.67
SBP3 *A. Alba*	0.0003	0.0690	0.0150	230.00	50.00	50.00
SCP3 *A. Alba*	0.0990	0.1100	0.0100	1.11	0.10	0.10

After determining the concentration of Hg in sediment and water and determining BCF and TF, after that make a model concept. The concept is made that can be translated by making a Causal Loop Diagram (CLD). Factors included in the CLD are the concentration of Hg in the sediment, concentration of Hg in water, Hg concentration in roots, BCF value, TF value (root to stem), and TF value (stem to leaf). CLD of Hg phytoremediation by *Avicennia alba* can be seen in **Figure 7.**

Figure 8 shows the results of the dynamic system of Hg metal phytoremediation by *Avicennia alba*. Based on the graph, it can be explained that the concentration of Hg in the soil will decrease due to the ability to extract heavy metal Hg by *Avicennia alba* (Figure 9 (a)). At the roots, the concentration of Hg also experienced the same thing in the soil (Figure 9 (b)). This is because the ability of translocation in the stem is greater than root extraction in absorbing Hg so that the accumulation of Hg in the root's decreases. The opposite condition occurs in the stems and leaves of Figure 9 (c) and (d). The concentration of Hg in stems and leaves increased because the TF value from root to stem was greater than the TF value from stem to leaf, so that the accumulation of Hg concentration in stems increased with time While the concentration of Hg in the leaves also increased, this was due to the presence of TF from stem to leaf. The higher the TF value from stem to leaf, the higher the Hg concentration in the leaves. Based on this, it shows that phytoextraction occurs in the phytoremediation process of Hg by *Avicennia alba*. The highest phytoextraction process occurred in the stem and was not balanced with the roots' extraction ability, which resulted in the reduced concentration of Hg in the roots.

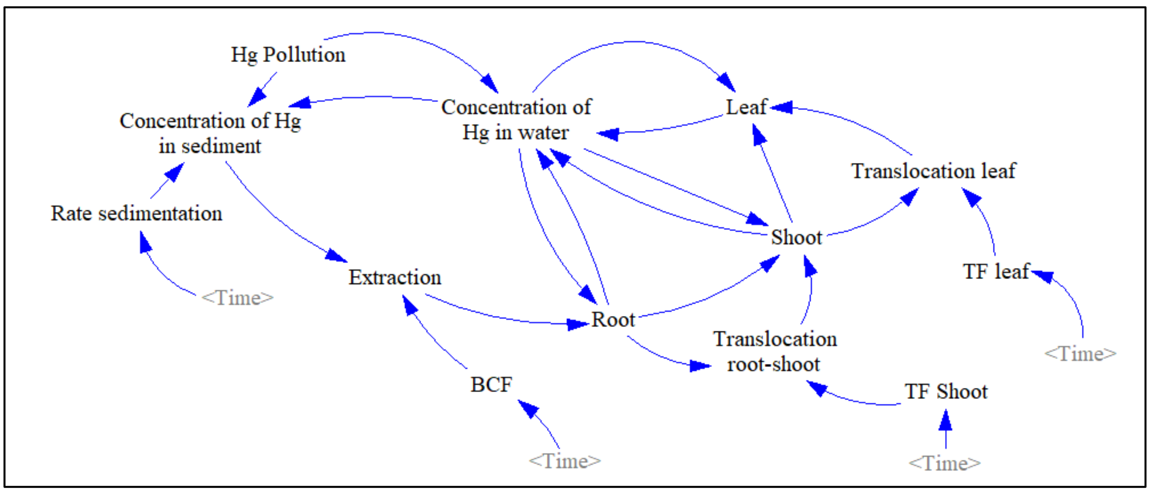

Figure 7. CLD Hg accumulation in *Avicennia alba*.

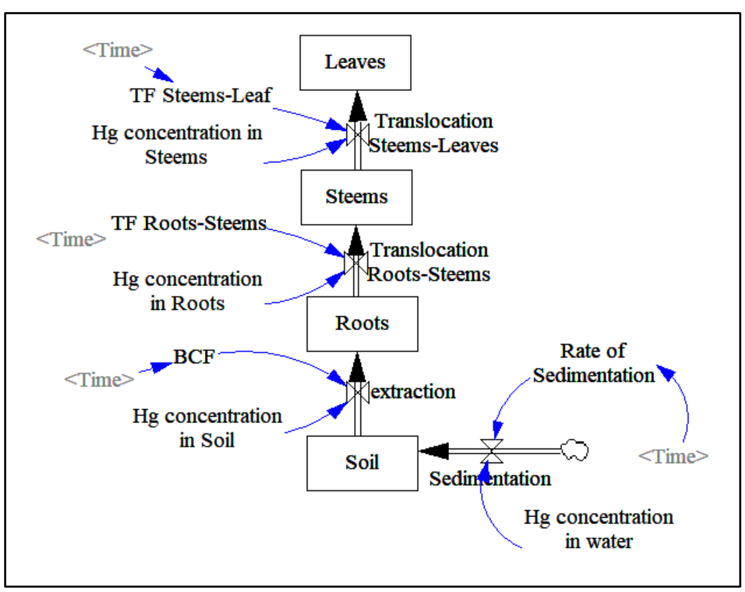

Figure 8. dynamic system Hg accumulation in *Avicennia alba*.

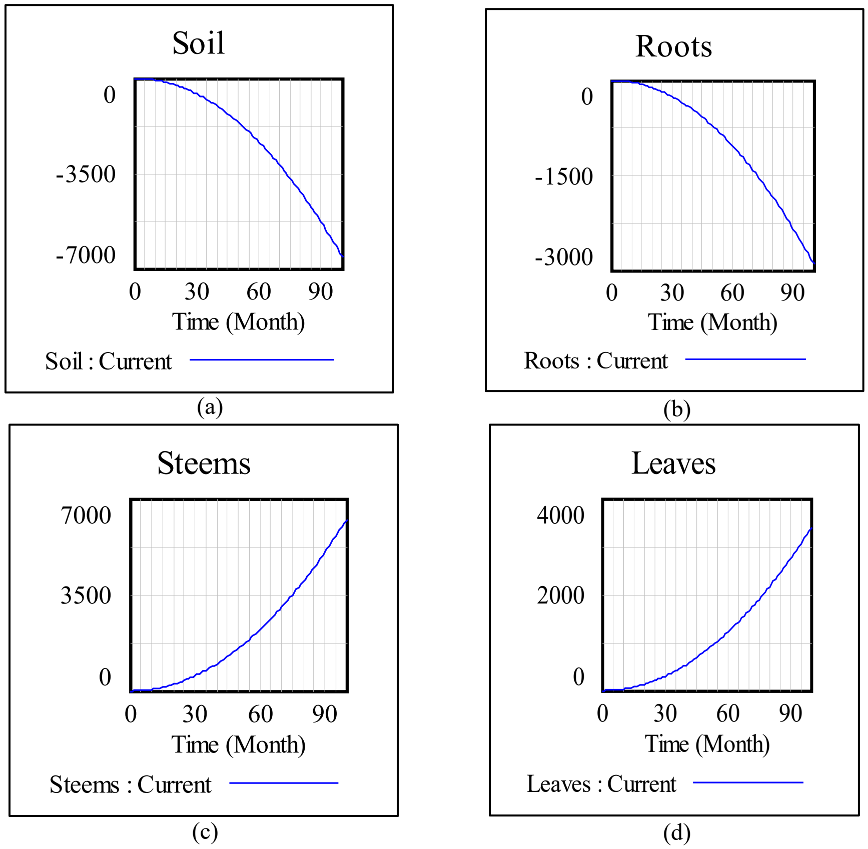

Figure 9. (a) Sedimentation of contaminant Hg in sediment, (b) extraction of contaminant Hg in root, (c) translocation of the contaminant of Hg in stems and (d) translocation of contaminant oh Hg in leaves.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this manuscript.

REFERENCES

1. Nawiyanto, E. C. Endrayadi., S. A. Handayani., D. Salindri., and I. Kumalasari. (2018) Menyelamatkan Nadi Kehidupan : Pencemaran Sungai Brantas Saving the Vein of Life : Pollution of Brantas River and Its Control in a Historical. *Patrawidya Seri Pnb. Penelit. Sej. dan Budaya* **19**(3), 3–11.
2. Central Statistic Agency. (2021) Jumlah Perusahaan Industri Besar dan Sedang Jawa Timur. Jakarta. pp. 1-51
3. Said, Nusa Idaman., Rita D., and Hartaja K. (2018) Kondisi Kualitas Air Baku Instalasi Ngagel Perusahan Daerah Air Minum (PDAM) Kota Surabaya the Condition of the Raw Water Quality of the Ngagel. *Air Indonesia* **10**(2), 52–66.
4. Barus. (2017) Analisis Kandungan Logam Berat Kadmium (Cd) dan Merkuri (Hg) pada Air dan Sedimen di Perairan Muara Sungai Banyuasin. *Maspari J.* 9(1), 69–76.
5. Gina, Oktavia. (2013) in *Analisis Kandungan Merkuri (Hg) pada Air dan Sedimen dengan Merkuri (Hg) pada Kerang Hijau (Perna Viridis) di Pesisir Tambak Wedi Surabaya*. Universitas Brawijaya, Malang. pp. 1-151
6. Sari, Syarifah Julianda., J. F. A. Kirana., and G. Guntur. (2017) Analisis Kandungan Logam Berat Hg dan Cu Terlarut di Perairan Pesisir Wonorejo, Pantai Timur Surabaya. *J. Pendidik. Geogr* **22**(1),1–9.
7. Nedjimi, Bouzid. (2021) Phytoremediation: a sustainable environmental technology for heavy metals decontamination. *SN Appl. Sci* **3**(3), 1–19.
8. Ardianti, Vega. (2017) in *Analisis ogam Berat (Zn) pada Mangrove Avicennia alba dan Sonneratia Caseolaris di Kawasan Mangrove Muara Sungai Porong Kecamatan Jabon Kabupaten Sidoarjo Jawa Timur*. Universitas Brawijaya, Malang. pp. 1-134
9. Mansawan, Lenny Binfun Saneraro. (2016) in *Fitoremediasi Logam Berat (Mn, Pb, Zn) dari Limbah Cair Laboratorium Kimia Universitas Kristen Satya Wacana oleh Kayu Apu Dadak (Azolla pinnata R.Br.)*,Universitas Kristen Satya Wacana, Salatiga" *Skripsi*, pp. 1–24.

10. Tangahu, Bieby Voijant., S. R. Sheikh Abdullah., H. Basri., M. Idris ., N. Anuar., dan M. Mukhlisin. (2011). A review on heavy metals (As, Pb, and Hg) uptake by plants through phytoremediation. *Int. J. Chem. Eng,* doi: 10.1155/2011/939161.

11. Ariadi, Bambang Yudi., M. Haeruman K., D. Rochdiani., and E. Rasmikayati. (2015). Model Dinamik Manajemen Usahatani Ubikayu. *Agrar. J. Agribus. Rural Dev. Res* **1**(1), 25–31.

12. Adipraja, P.E.E., and D. A. Sulisty. (2018) Pemodelan Sistem Dinamik untuk Prediksi Intensitas Hujan Harian di Kota Malang. *J. Ilm. Teknol. Inf. Asia* **12** (2), 137

13. Khodijah, N.S., R. A. Suwignyo., M. U. Harun., and L. Robiartini. (2019) Phytoremediation potential of some grasses on lead heavy metal in tailing planting media of former tin mining. *Biodiversitas* **20**(7), 1973–1982

14. Yashim, Z.I., O. Kehinde Israel., and M. Hannatu. (2014) A Study of the Uptake of Heavy Metals by Plants near Metal-Scrap Dumpsite in Zaria, Nigeria. *J. Appl. Chem* **2014**,1–5

15. Octaviani, Shinta., E. Suryani. (2014). Simulasi dan Pemodelan Sistem Persediaan Pada Perusahaan Retail Dengan Metode Sistem Dinamik (Studi Kasus : Distribution Center Hypermart Surabaya). *Jurnal Teknik POMITS* **1**(1), 2–7.

16. Sterman, John. (2005) *The energy transition and the economy: a dynamic systems approach*.

17. Subiantoro, Sigit. (2007). Kombinasi Preventive dan Reactive Maintenance dengan Simulasi Sistem Dinamik. *Mesin* **9**(2), 86–97.