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APPROACH OF DYNAMIC SYSTEM IN LEAD PHYTOREMEDIATION ON MANGROVE *Avicennia alba*

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Abstract

Lead occurs naturally in nature at low concentrations. Its concentration increases in the presence of other lead pollutant sources. It has high toxicity and harms to the environment (soil, air, and water) and humans. Handling heavy metal pollution in waters by utilizing local plants, including mangroves, has been widely reported. Mangroves is a potential phytoremediation agents. The aims of the study was to determine the dynamics system of the accumulating Pb by *Avicennia alba* based on the value of the bioconcentration factor (BCF) and the value of the translocation factor (TF). The sampling location was at Wonorejo Mangrove Forest Ecotourism in Surabaya. Samples were taken in the form of water, sediment, roots, stems, and leaves of *A. alba* and those samples were analysed to detect Pb concentration using atomic absorption spectrophotometer (AAS). The results showed that the average concentration of Pb in water were 0.1 mg/L to 6 mg/L. The average concentration of Pb in the sediment were 0.1 mg/kg to 7.59 mg/kg. The Pb sedimentation process can be shown based on the higher Pb concentration in the sediment than Pb concentration in the water. Based on the data and dynamic system modeling, there was a relationship between all components of *A. alba* with environmental media. The phytoremediation processes of Pb metal by *A. alba* were sedimentation, phytostabilization, and phytoextraction. *A. alba* has potentially as a phytoremediator in polluted coastal areas.

INTRODUCTION

Environmental Pollution is the entry or inclusion of living things, substances, energy, and other components into the environment by human activities so that they exceed the established environmental quality standards [1]. Surface water sources are one of the environmental media entering by pollutants that impact lowering water quality. Contamination from organic and inorganic elements, like heavy metals. Heavy metal concentrations in rivers can affect the death of aquatic biota, both at high and low concentrations. Heavy metals first undergo the accumulation process in the body of biota at low concentrations [2].

As a non-essential heavy metal, lead (Pb) is naturally present in nature through natural and artificial processes at

low concentrations [3]. The presence of Pb in waters naturally through crystallization of it in the air with the help of rainwater [4]. Lead decomposes over a long period in environmental media, and its toxicity does not change [5]. The source of lead is from activities using fossil fuels, mining, and manufacturing. Manufacture of batteries, ammunition using lead as material. Metal products such as solder and pipes, and X-ray protective devices tool. Products such as gasoline, paint, and pipe solder contain lead [6]. The presence of lead in water, air and the entry of lead in the food chain allows leading to accumulate in the human body. Lead (Pb) has high toxicity to humans because of the accumulation process that can damage brain development in children, blockage of red blood cells, anemia, kidney damage, muscle pain and weakness, nausea, abdominal pain

[7]. That fact had attracted the attention of many researchers, especially in dealing with river pollution caused by the presence of lead.

Mangrove forests are in a transitional area between terrestrial and marine ecosystems. It has a mud substrate, calm water, and the sea waves are not too big [8]. The intensity of seawater inundation affects the composition of mangrove vegetation. Functioning biologically in supporting coastal ecosystems, mangrove forests also have a chemical function to neutralize waste and accumulated chemicals that enter the waters [9]. This vegetation has a height ranging from 5-25 m, depending on age and location. Mangrove roots function to hold sediment not directly to enter the sea [10]. Mangroves also serve as a breakwater for seawater and an ecological function, namely absorbing, transporting, and storing heavy metals around the environment where they grow, accumulating in roots, stems, and leaves. The transferor accumulation of heavy metals from sources to parts of mangrove plants is possible because of the translocation ability possessed by several mangrove species [11]. Bengen [12] reported that several mangrove species can live in areas with high salinity, it was 2 to 22‰ (brackish water) to salty up to 38‰ of salinity. Every kind of mangrove tolerates salinity levels in different ways. Some of them will secrete salt in the leaf glands, and others will inhibit the absorption of salt from the growth medium [13].

There was at least one essential or dominant actual plant belonging to 4 families: *Rhizophoraceae* (*Rhizophora*, *Bruguiera*, and *Ceriops*), *Sonneratiaceae* (*Sonneratia sp.*), *Avicenniaceae* (*Avicennia sp.*), and *Meliaceae* (*Xylocarpus sp.*) at mangrove forests in Indonesia [5]. Except for the genus *Meliaceae*, the other three genera are in the territory of Indonesia [14]. Genus *Avicennia* with pencil-shaped roots protruding from the water surface that function as breath roots formed from the expansion of horizontal roots [15]. *Avicennia marina* known as api-api putih and *Avicennia alba* known as api-api hitam in Indonesia [16, 17].

The estuary of the Wonorejo River, which is part of the coastal area of East Surabaya, has narrow waters and is bordered by the Madura Strait. It is a canal from the Jagir River, which carries industrial waste, including sediment supply, empties into the Wonorejo River's estuary. The fine silt and deep blackish layers seen at low tide are evidence of the accumulation of these sediments. Mangroves dominate the ecosystem in this area. The thickness of the mangrove vegetation in this area ranges from 15-20 meters inland [10, 18, 19]. The types of mangroves around the Wonorejo River include *Avicennia marina*, *Avicennia alba*, *Excoecaria agalloch*, *Avicennia officinalis* [20]. Two types of *Avicennia* with a high population in the Wonorejo Mangrove Forest Area are *Avicennia marina* with 88% and *Avicennia alba* with 11% of the total mangrove population. This area was planted with mangroves ten years ago [21].

Phytoremediation as a water treatment technology by utilizing plant species tolerant to Pollution, with a high population and biomass, is the suitable method to be used

and investigated further [2]. There are three mechanisms of absorption and accumulation of heavy metals by plants: root uptake, translocation of heavy metals from roots to stems and leaves, and localization of heavy metals in cells and tissues [22]. Many studies reported the phytoremediation of heavy metals by mangroves. Mulyadi et al. [19] reported concentration of Cu in *Avicennia sp.* roots at the Wonorejo estuary reached 5.6 ppm. Another study by Hamzah and Setiawan [23] showed that the roots and leaves of *Avicennia sp.* contained 13.08-37.68 ppm and 7.08-10.07 ppm of Cu, while the Pb content in the roots and leaves at 57.52 – 59.16 ppm and 61.93 – 64.32 ppm, with average values of BCF and TF for Cu were higher than 1 while BCF and TF for Pb also were higher than 1 at Muara Angke, Jakarta. *Avicennia alba*'s robust root system allows it to absorb heavy metals from sediment and water. Other studies about *A. alba* in Wonorejo Mangrove Forest showed that the average concentration of Cr in *A. alba* roots ranged from 25.4 to 55.3 mg/kg and ranged from 60 to 79.3 mg/kg in the sediment. The BCF values in *A. alba* were 0.32 to 0.83 mg/kg, *A. alba* showed potential as a moderate accumulator for Cr [21]. According to Titah et al. (2021) [24], the average concentrations of Cu reached 94.0 ± 79.2 mg/kg at Wonorejo coastal area. *A. marina* could uptake metals and the accumulations of Cu was 110 ± 10.4 mg/kg. However, the highest accumulation by *A. alba* reached 90.8 ± 24.7 mg/kg for Cu.

In the 2017-2019 period, several studies on the accumulation of heavy metals by several types of mangroves in the Wonorejo river, Surabaya was reported. Based on Febriana (2017) [25] about the accumulation of Pb in the *Avicennia marina*. Pb concentration in roots was 5.67 to 6.61 mg/kg and 9.58 to 10.28 mg/kg accumulated in the leaves. The sediment Pb concentration was 4.96 to 6.42 mg/kg. The value of BCF and TF were higher than 1, which indicated that *A. marina* was an accumulator of heavy metal Pb. Yuliardhan (2019) [26] reported the difference results in the accumulation of Pb by *Rhizophora mucronata*. The range of accumulation in the roots was 0.006-0.008 mg/kg, with a Pb concentration value in the sediment 17.19-22.335 mg/kg and the BCF value <1. Pb translocation in *Avicennia alba* was more than 1, where TF value was below BCF value (34). Pb concentrations in sediment ranged from 14.49-20.79 mg/kg, 3.28-4.71 mg/kg in roots, and 5.19-7.09 mg/kg in leaves. The Pb concentration in the sediment is higher than in the tissue because the mangrove roots prevent the entry of heavy metal contaminants [32]. The differences in accumulation of each mangrove species may be caused by the accumulation ability of each species and the difference of growing locations in the Wonorejo river and estuary. Based on Luthanza et al. (2021) [28], the highest average Pb concentration for waters and sediments was obtained at stations C and A at the Wonorejo Mangrove area, with values of 0.069 mg/L and 4.22 mg/kg, respectively. The highest values of TF for both roots to stems and to leaves in the accumulation of Pb were also discovered in *Avicennia lanata* and *A. alba* mangroves, respectively.

A dynamic system model, an alternative tool, is used to determine the dynamics that occurred in the phytoremediation process by mangrove plants. A dynamic system model has also been applied with systems thinking more generally in various sustainability plans, including water resources and energy management. Forrester developed system dynamics in 1961 and 1969. Senge, in 1990, used Causal Loop Diagrams (CLDs), Archetypes, and quantitative methodologies to analyze system behavior through time and make the system more detailed than before [29]. The difference between dynamic systems and statistical models is that dynamic systems can get better predictions in the long, medium, and short term use as a reference for better decision making [30]. This study aims to determine the dynamics system of *A. alba* ability at the Wonorejo Mangrove area to accumulate Pb through value of bioconcentration factor (BCF) and translocation factor (TF).

MATERIALS AND METHODS

Sampling Location

As shown in Figure 1, the sampling location is in the Wonorejo Mangrove Forest Ecotourism Area, Wonorejo, East Surabaya, Indonesia. The sampling coordinates are in Table 1.

As shown in Figure 1, there are three sampling points, namely Station A, Station B and Station C. Station A is a station directly near to the estuary river, Station A is the starting point for the entry of pollutants into the sea; station B is a station between stations A and C. Station C is the station with the farthest location from the pollutant source and directly near the sea.

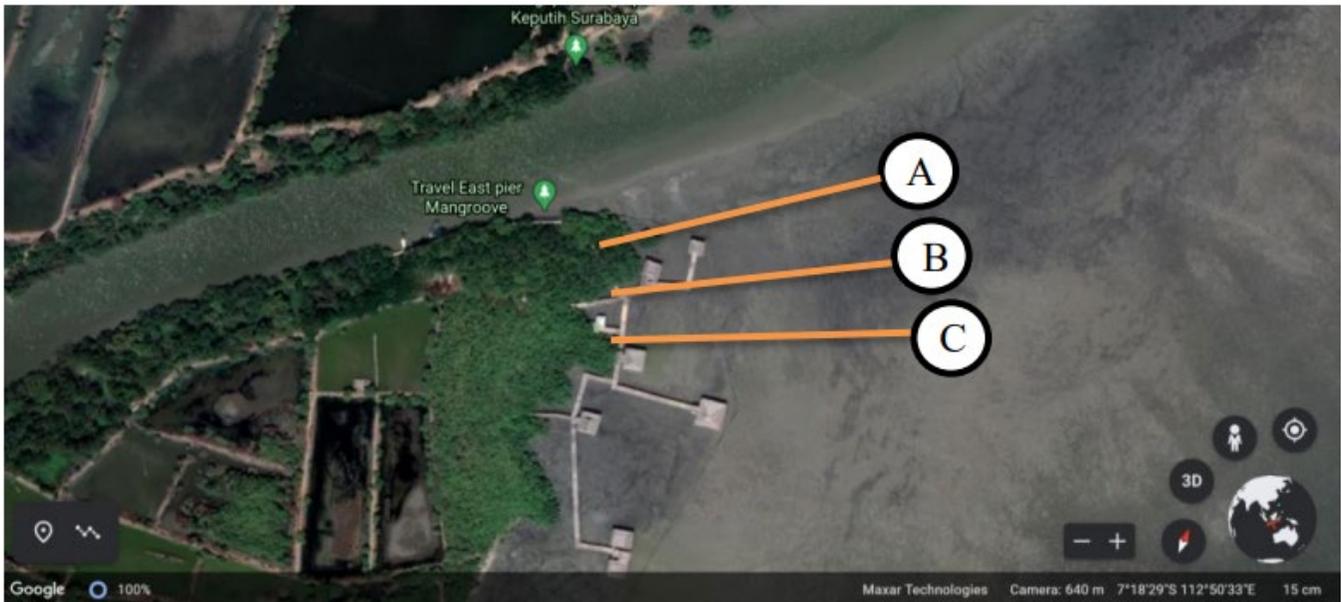


Figure 1. Sampling location (Google Earth, 2020).

Table 1. Point samplings coordinate.

No.	Location	Code	Information	Coordinate
Station A				
1	Plot 1	SAP1 <i>A. alba</i>	Sample <i>A. alba</i> Station A, Plot 1	SS 7°18'19.75" E 112°50'39.4"
2	Plot 2	SAP2 <i>A. alba</i>	Sample <i>A. alba</i> Station A, Plot 2	SS 7°18'20.21" E 112°50'39.05"
3	Plot 3	SAP3 <i>A. alba</i>	Sample <i>A. alba</i> Station A, Plot 3	SS 7°18'20.56" E 112°50'38.23"
Station B				
4	Plot 1	SBP1 <i>A. alba</i>	Sample <i>A. alba</i> Station B, Plot 1	SS 7°18'20.19" E 112°50'40."
5	Plot 2	SBP2 <i>A. alba</i>	Sample <i>A. alba</i> Station B, Plot 2	SS 7°18'20.39" E 112°50'39.92"
6	Plot 3	SBP3 <i>A. alba</i>	Sample <i>A. alba</i> Station B, Plot 3	SS 7°18'20.53" E 112°50'39.64"
Station C				
7	Plot 3	SCP3 <i>A. alba</i>	Sample <i>A. alba</i> Station C, Plot 3	SS 7°18'21.98" E 112°50'39.52"

Materials of Sampling

The sampling tool needed in this study was a Global Positioning System (GPS) GPSmap 76CSx (Garmin, USA) for determining the coordinates of the sampling point. Others sampling tools were hand drills to take sediment, machete samples of stems and leaves, raffia as a marker sampled mangroves. Some plastic bottles and plastic clips were brought as containers to put samples, a cool box was as a place to store samples temporarily before being brought to the laboratory. Others things were some ice cubes as a sample preservative, stationery and camera as a medium for recording and documenting, pH meter as a soil pH tester, thermometer as a temperature tester, refractometer as a salinity tester, a meter to measure.

Methods of Sampling and Analysis

The transect quadrat sampling method was used in this study because the transect quadrat sampling method was suitable. The dimensions of one quadrant are 10m x 10m, determination of sampling points was conducted using GPS. The root, shoot, and leaf mangrove plant samples and sediments were prepared before analysis. Analysis of Pb concentration was conducted using an atomic absorption spectrophotometer (AAS). All samples of mangrove parts were dried at 105°C for 24 hours. The dry samples were extracted using a modified wet digestion method based on [31]. The EPA 3050B method (1996) to carry out sediment extraction [32]. All samples were analyzed using AAS to

measure Pb concentrations in sediment, water, and roots; shoots; leaves of *A. alba* at accredited Sucofindo Laboratory in Surabaya.

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

This calculation aim was to determine the occurrence of metal accumulation in mangroves by calculating the metal content in the sediment and roots. BCF in roots was used to determine how much metal content in roots came from the environment [33]. The formula for calculating BCF was as follows:

$$BCF = \frac{\text{Concentration in mangrove organ}}{\text{Pb media concentration in sediment}} \quad (1)$$

According to Baker (1981) [34], the BCF has three categories, i.e accumulator if $BCF > 1$, indicator category if $BCF = 1$, and the last, the excluder category if $BCF < 1$.

Translocation Factor (TF) is the ratio value of heavy metal content in leaves and roots. The TF value determines the transfer of accumulated metal from roots to leaves [35]. The formula can calculate TF:

$$TF = \frac{\text{Pb in shoot}}{\text{Pb in root}} \quad (2)$$

$$TF = \frac{\text{Pb in leaves}}{\text{Pb in shoot}} \quad (3)$$

According to Majid et al. (2014) [36], the TF value has two categories, i.e if the $TF > 1$, then it was included in the phytoextraction mechanism. Value of $TF < 1$, it was included in the phytostabilization mechanism.

Dynamic System

The dynamics system approach begins by defining the problem dynamically. Make a concept of a real system that contains variables that are mutually related. The initial concept can be poured into a Causal Loop Diagram (CLD). Once the CLD has been conceptualized, it is next to identify independent stocks or accumulations in the system and their inflows and outflows. The identification is formulated in a behavioral model that is able to reproduce dynamic problems within a predetermined scope. An approach refers to qualitative Causal Loop Diagrams (CLDs) and quantitative methodologies to analyze system behavior through time. It uses CLD as a graphical tool to understand the relationship between system components. Then, proceed with quantitative analysis using Stocks and Flows Maps (SFM) on Dynamics System software package developed based on CLD. The analyst built the simulation model to evaluate the system's behavior under several scenarios or virtual environments through this qualitative modeling phase [29]. The symbols contained in the sub-model diagram were rectangles that represent stock (level), valve symbols that represent flow (rate or decision point), and symbols for writing complementary variables [29]. Sub-model diagramming in this study used Vensim software.

The stages of dynamic system modeling were as follows:

1. Concept generation
The first step was to identify the problem and then look for actors dealing with the problem and the causes. The next stage is to create a mental pattern or model by using the information in CLD.
2. Modeling
Based on the formed CLD, using software to make Stock Flow Diagram (SFD) symbols.

3. Enter Data
Data were entered into the model in various forms, i.e., as stock, like flow, in addition, and can also be constant
4. Model Simulation
The model simulation started with determining the time, the integration method, and the time steps. So that the graph of the behavior of time could be obtained.
5. Model validation
The model must go through the stages of model checking following applicable principles [36, 37].

RESULTS AND DISCUSSION

Figure 2 showed the concentration of Pb in sediment at all points of sampling locations. Data showed that the concentration of Pb has a different value in each station. The Pb concentration was 5,4 to 9,4 mg/kg at Station A; it was 0,1 to 2,9 mg/kg at Station B and it reached 1,4 mg/kg at Station C. Station A was the nearest station to the sea, the high Pb concentration in the sediment due to come from spills or paint residue that was used on fishing boats. In addition, the adsorption process affected the presence of metals in the estuary. Adsorption was a process when a fluid/liquid or gas was bound to a particle. The adsorption process occurred in the water column. The suspended sediment could adsorb heavy metals in the dissolved phase when the material experiences deposition to the bottom [38].

Figure 3 showed the concentration of Pb in water at all points of sampling locations. The data showed a difference in the concentration of Pb in the sediment. The highest concentration of Pb in water were detected at station B with a range of 3.7 to 6 mg/L. The exact concentration values were shown at stations A and B, ranging from 0.1 to 0,2 mg/L. Comparing the concentration of Pb in the sediment at station B, the Pb content in the water has not been absorbed into the sediment. The Pb concentration in the water was greater than the Pb concentration in the sediment.

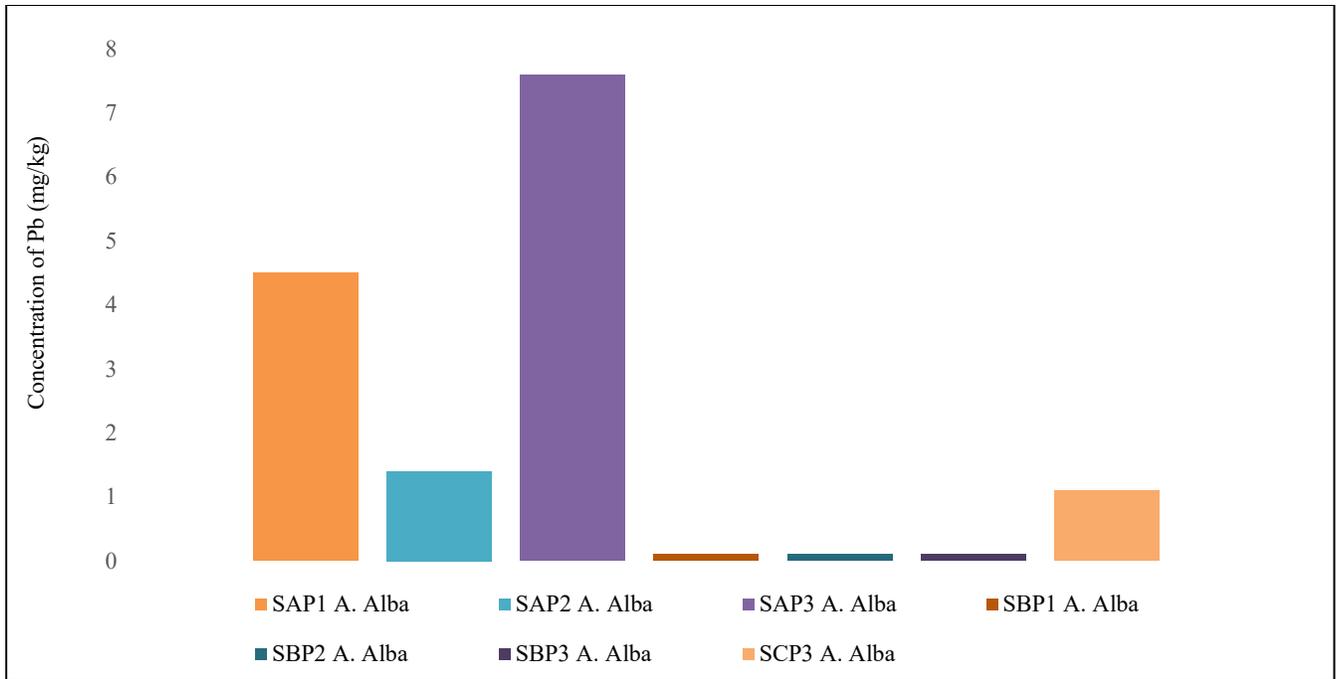


Figure 2. The concentration of Pb in sediment at all points of sampling locations.

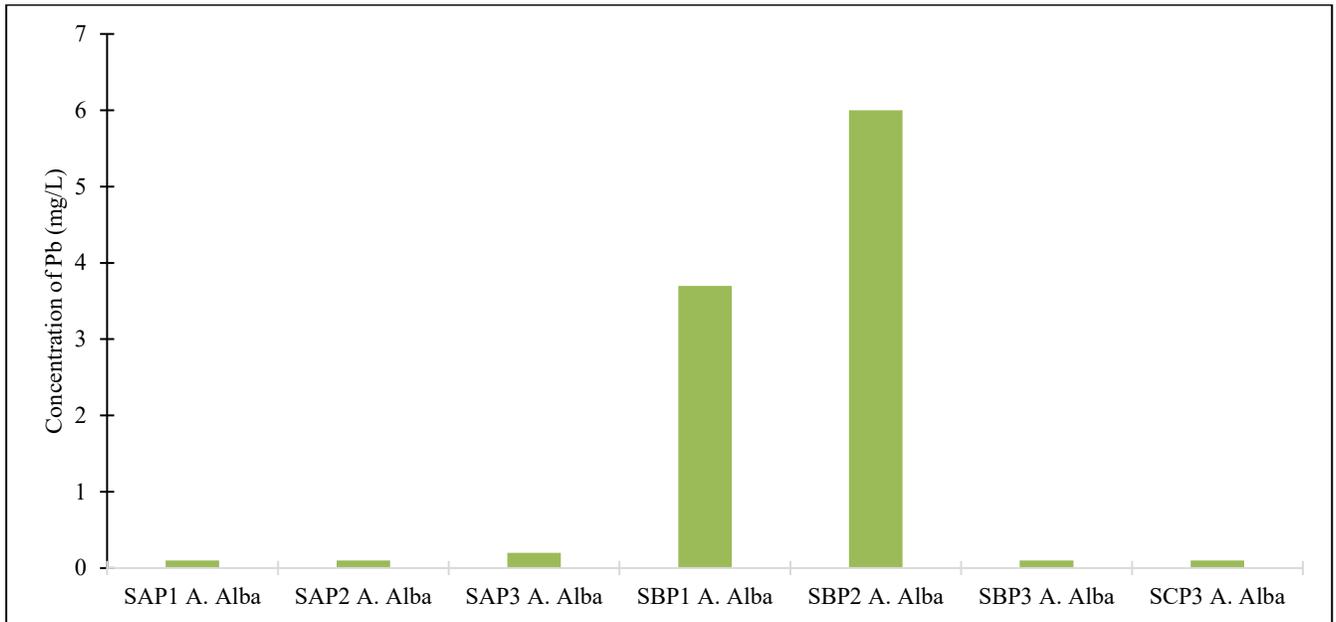


Figure 3. The concentration of Pb in water at all points of sampling locations.

Figure 4 showed the BCF value of *A. alba* on Pb. It was calculated based on equation 1. The value at stations A were 0.1, 0.1, 0.2, and at the station C was 0.1. The BCF value at both stations was < 1 , it indicated that *A. alba* was a plant excluder for Pb. The excluder was a property where plants have limited heavy metals absorption in their environment, both sediment, and water. However, when they enter the plant body, heavy metals can be ready to translocate to other body parts or the above biomass [39]. The BCF value was

3.7, 6, 0.1 at Station B. The BCF values were generally > 1 so that *A. alba* at station B was an accumulator. The TF values were calculated based on equations 2 and 3. Based on Figure 5, the average TF values were more than 1 at almost all points of sampling locations. It indicated that the plant can translocate heavy metals from roots to other organs. The situation explained that the Pb phytoextraction mechanism occurred in Pb phytoremediation by *A. alba*.

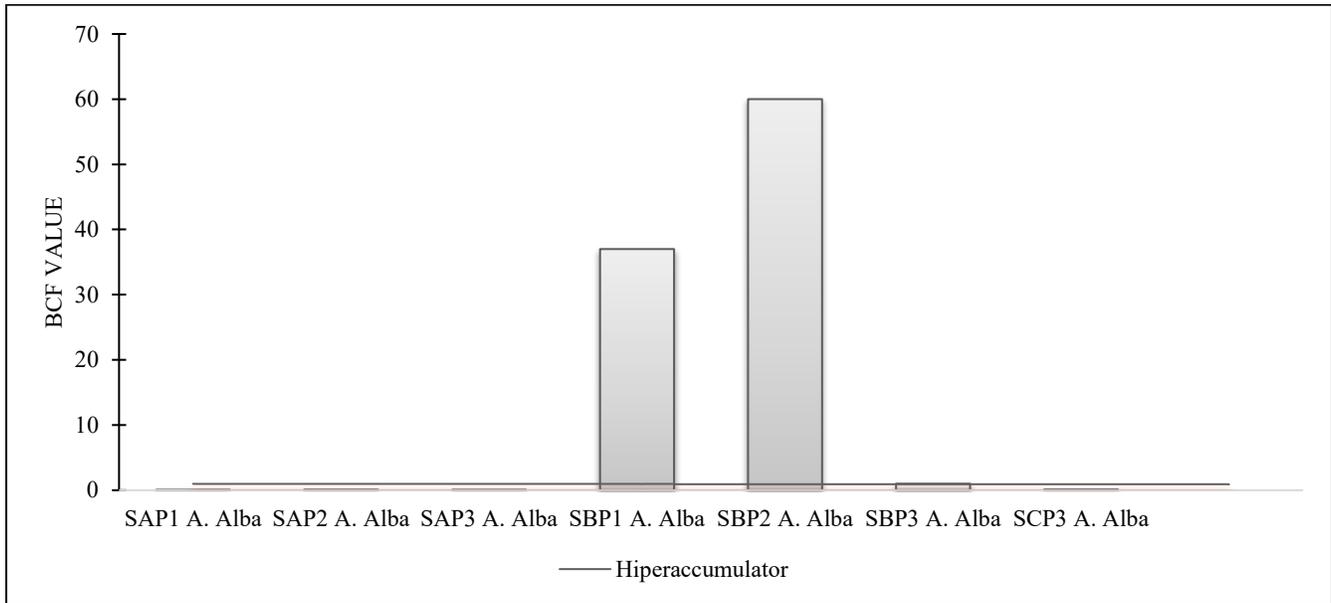


Figure 4. BCF value of Pb in *A. alba*.

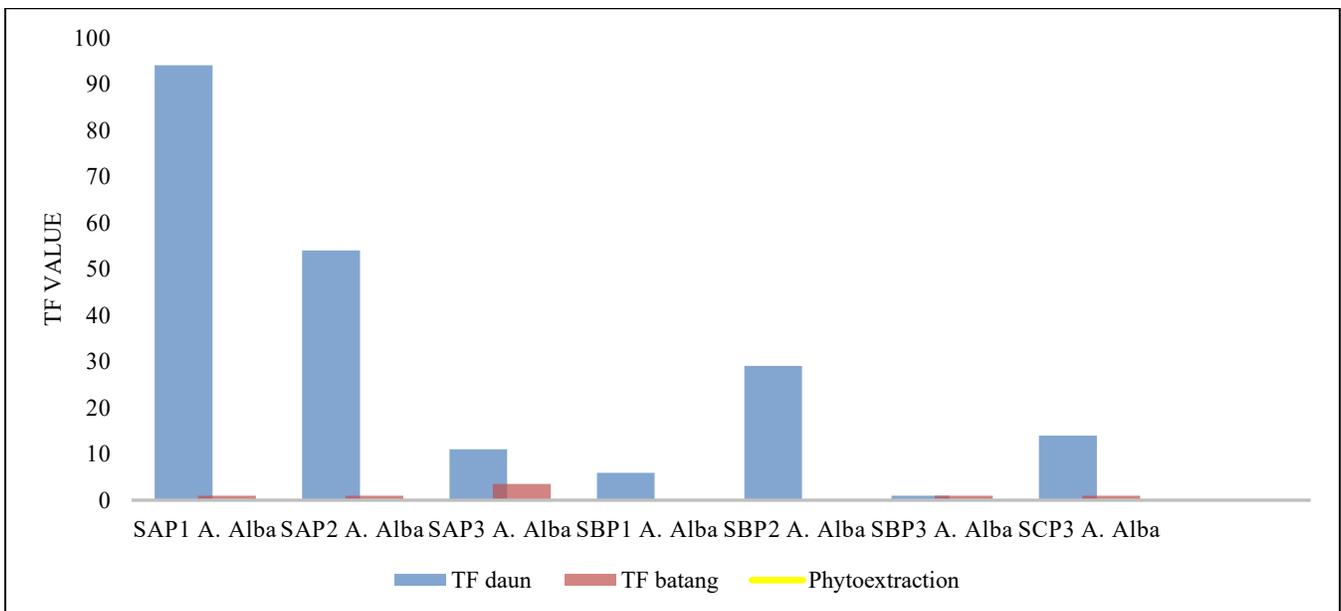


Figure 5. TF value of Pb in *A. alba*.

Figure 6 showed a causal relationship between the components in the Pb phytoremediation process by *A. alba* plants. The relationship between the existing components, both in plants and other components from outside the plants were arranged. The mechanism was then entered into a dynamic model to determine the relationship between these components and time. Figure 7 depicted the sequence of the phytoremediation processes and their correlation with the previously BCF and TF values. The modeling produced a relationship between each process that occurred in each part of the plant with time. Figures 8, 9, 10, and 11 represented the resulting model data and mathematical equations enrolling into the dynamic system, and the system executes. The results showed that *A. alba* was included in the accumulator category, as shown in Figure 9. The ability of this plant to absorb Pb from sediments increased with time. The phytoextraction process in the stems of *A. alba* decreased over time (Figure 10), but the phytoextraction

processes in the leaves increased over time. The phytoextraction process occurred from roots to leaves (Figure 11), it increased with time. Based on TF values of leaves, it was higher than 1. The high TF value for non-essential metals (Pb) was caused by the high mobility of metals from roots to leaves. Mangroves plants tended to translocate more essential metals than non-essential metals [35]. Non-essential metals did not affect the metabolic process of mangroves, so that non-essential metals were absorbed and stored in certain parts to degrade metal toxicity.

Based on the data and dynamic system modeling, the relationship between all *A. alba* and environmental media components was shown. The sedimentation, phytostabilization, and phytoextraction processes in the Pb phytoremediation process occurred on *A. alba* plants. *A. alba* plants can be a phytoremediator in polluted river areas and coastal areas.

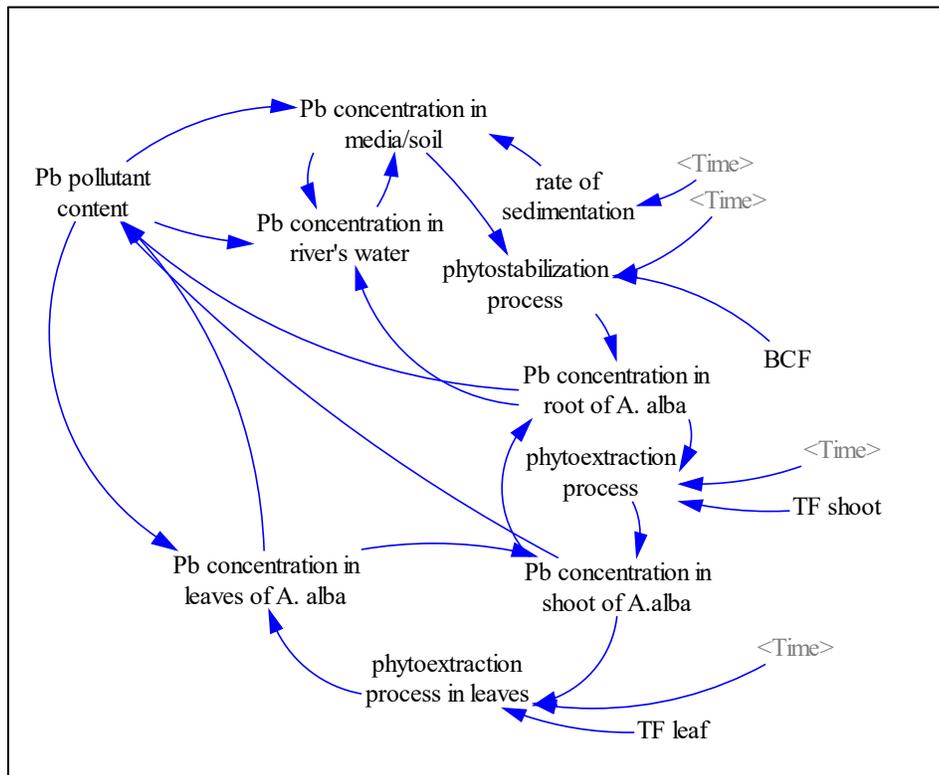


Figure 6. C.L.D. phytoremediation of Pb by *A. alba*.

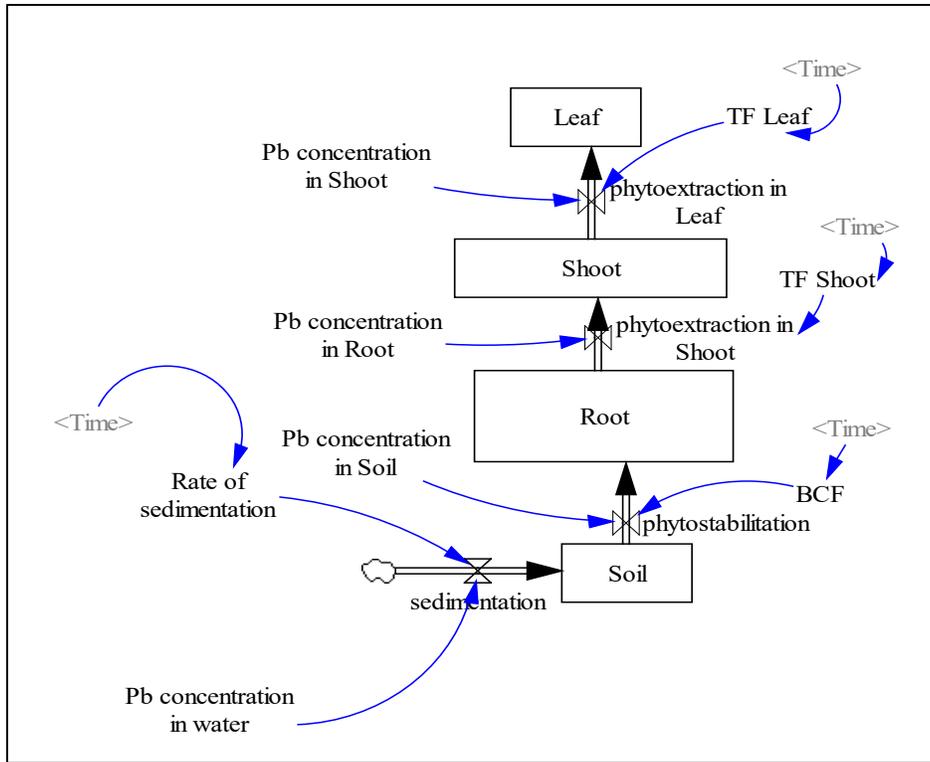


Figure 7. Dynamic System of Pb phytoremediation by *A. alba*.

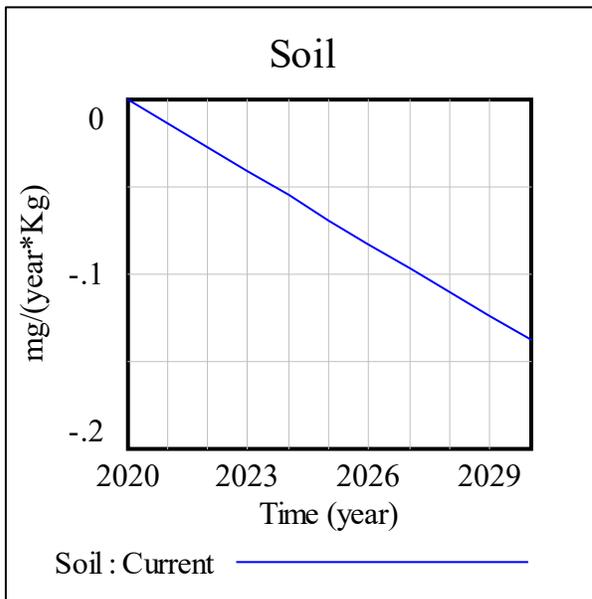


Figure 8. Sedimentation of Pb in media.

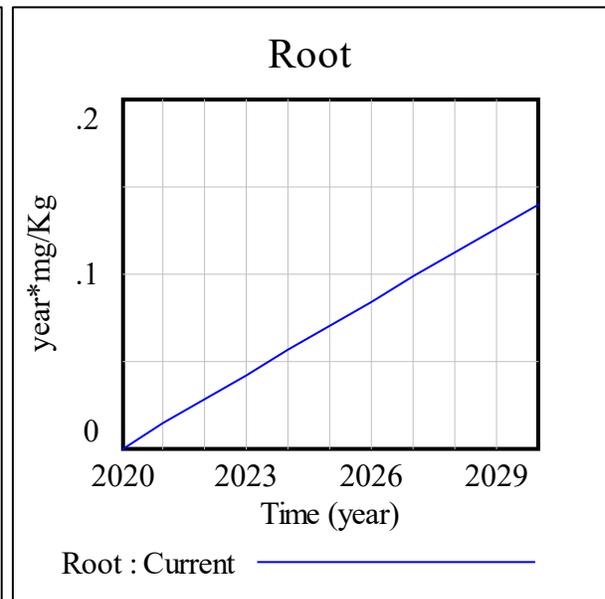


Figure 9. Phytostabilization of Pb in root.

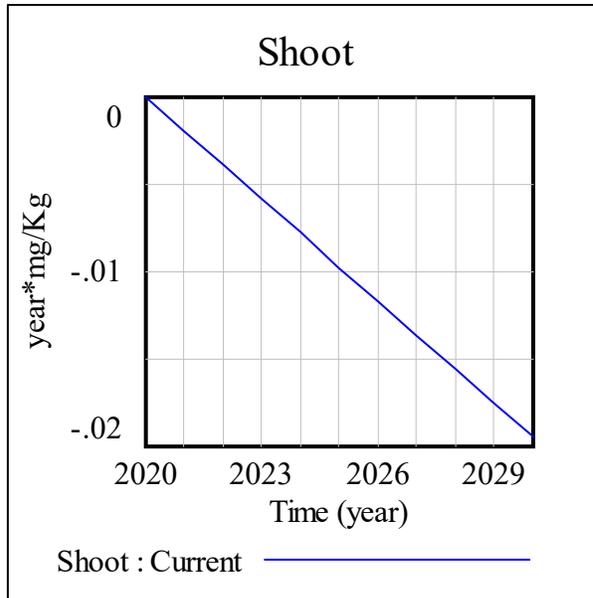


Figure 10. Phytoextraction of Pb in the shoot.

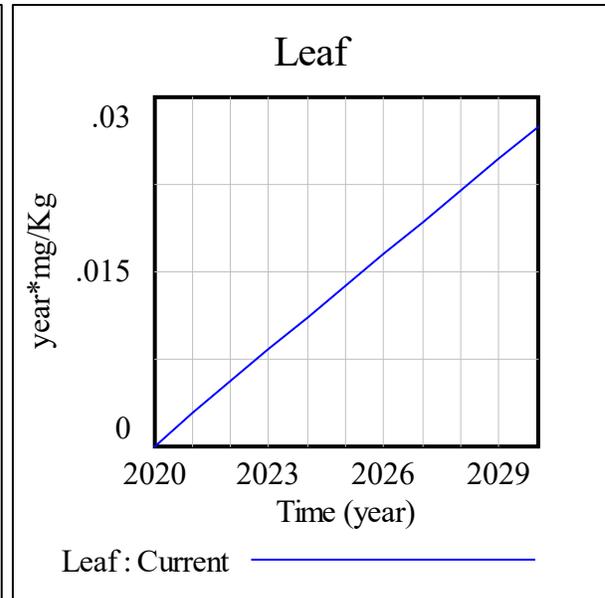


Figure 11. Phytoextraction of Pb in leaf.

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CONFLICTS OF INTEREST

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

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