A decrease in the activity of Hg\(^{2+}\) due to the provision of humic acid and fulvic acid onentisols polluted by heavy metals of mercury

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Abstract. Analyze the decrease of the concentration of heavy metals Hg\(^{2+}\) on entisols polluted by mercury due to the provision of humic acid and fulvic acid of Tithonia diversifolia. There are nine levels: With no humic acid and fulvic acid treatments (FVA0); 50 ml of fulvic acid per kg\(^{-1}\) soil (FA50), 75 ml (FA75), 100 ml (FA100), 125 ml (FA125), 50 ml of humic acid per kg\(^{-1}\) soil (HA50), 75 ml (HA75), 100 ml (HA100), and 125 ml (HA125). The concentration of Hg\(^{2+}\) in entisol was measured by means of Mercury Analyzer (AAS). The results revealed that regarding mercury content in the soil, fulvic acid had a better effect on the change of Hg-chelate compared with humic acid. Fulvic acid was able to increase Hg-chelate up to 96.58%, whereas humic acid by 83.06% at a dose of 125 ml kg\(^{-1}\)entisols for 40 days of incubation.

1. Introduction

Humic and fulvic are organic compounds found in organic materials, serving an essential role in the quality of the soil and nutrient availability. Organic waste from farming is usually given to the soil in the form of compost, containing humic and fulvic compounds [1]. These humic and fulvic compounds are end products of the organic decomposition process and playing a pivotal role in the improvement of soil fertility. The role of the humic compound on soil fertility, able to restore soil structure, increase the capacity of holding groundwater and increase the capacity of soil cation exchange (CEC), as well as able to decrease the solvability of toxic substances like Fe and Al [2]. The humic compound had an influence on the mobilization of various nutrients, particularly phosphate in the soil [3].

Research on phytoremediation can be an alternative in lowering the toxicity level of heavy metals in the environment [4]. It is also true with the Impact of industrial waste like gold extraction efforts that use mercury substances. However, information is still lacking regarding to the mapping of pollution level caused by mercury in the soil and its lessening content in plants that had been given with organic substances on the soil that had been polluted with mercury. One way to recover the soil that had been polluted with heavy metal mercury can be in the form of adding more organic substances in the area around the plant or crop rooting.

The source of organic substances that are frequently used for soil recovery is Tithonia diversifolia pruning [5]. Tithonia diversifolia is a weed from Asteraceae group, which can be found in every area in Indonesia. Not only having high potential for providing N and P, but the organic substance in Tithonia diversifolia also contains fairly high humic acid and fulvic acid that is able to decrease the toxic
nature of some heavy metals.

The decomposition of organic materials generates organic compounds that have low molecule weight yet highly reactive, such as humic acid and fulvic acid. Phenolic acid and its derivatives, as well as benzene-carbochelate compounds, are the main building blocks of humic acid and fulvic acid. Humic acid has the more stable association between building blocks compared with fulvic acid, as in humic acid, there are more bonds of C–O and C–C in addition to the bond bridge of O and N. Humic acid is a complex compound of lignoproteins that plays a significant role in soil reactions like increasing soil’s Cation Exchange Capacity, clay translocation, bearing capacity, and also the surface area of absorbing heavy metal [6]. This substance also serves as a stimulant for plant growth and fixes the nature of soil physics, especially soil aggregates, hence lead to better water aeration and transportation [7].

Organic acids in the soil are able to bind excessive metal ions or toxic substances, thus lowering their number in entisols based on what the plants need. Most of the organic metal chelates are insoluble, and this phenomenon is essential in keeping the quality of the environment by decreasing the toxicity posed by heavy metals on plants, livestock, and human [8].

Therefore, this study was aimed to analyze the ability of humic acid and fulvic acid of Tithonia diversifolia compost in lowering the mercury concentration in the entisols polluted by mercury.

2. Methods

2.1. Types of research
This study was experimental research by using a Completely Randomized Design (CRD) comprised of 9 levels, and each treatment was repeated three times, so allowing 27 units of the experiment. The incubation level was: With no humic and fulvic acid treatment (FVA0), 50 ml fulvic acid per kg soil (FA50), 75 ml fulvic acid per kg soil (FA75), 100 ml fulvic acid per kg soil (FA100), 125 ml fulvic acid per kg soil (FA125), 50 ml humic acid per kg soil (HA50), 75 ml humic acid per kg soil (HA75), 100 ml humic acid per kg soil (HA100), 125 ml humic acid per kg soil (HA125).

This research was conducted in the laboratory and glasshouse of the Faculty of Agriculture, Universitas Tadulako, in 2017.

2.2. Data collection
Hg$^{2+}$ concentration in soil solution was measured until the 40th day with 5 days interval by using Mercury Analyzer (AAS), a method guided by Mercury Analysis Manual. Extraction of humic and fulvic compounds was adopted from “The International Humic Substances Society (IHSS)”. Supporting variable was also measured, i.e., initial soil analysis that encompassed soil pH (H$_2$O and KCl) was set with the suspension of 1:2.5 by means of the glass electrode, C-organic by using Walkey & Black method. Meanwhile, as the source of compost, a ±10000 g Tithonia diversifolia pruning was taken. It was then composted by means of decomposer for ± one month. Thereafter the ripened compost was extracted with 0.1 N NaOH for its humic and fulvic acids.

2.3. Statistical analysis
Data analysis was performed by using F-test at confidence level of 95% (α = 5%) and 99% (α = 1%) respectively. Regression analysis was employed to figure out the close-knit relationship and form of the relationship between treatments and variables being observed.

3. Results and discussion

3.1. The characteristic of experiment soil
Mercury-polluted soil as the growing media had sandy loam texture with each fraction distribution was sand (17.43 %), dust (78.33 %), and silt (4.24 %), as to bulk density was 1.21 g cm$^{-3}$. In terms of chemical nature, it had pH H$_2$O of 6.90 and pH KCl of 6.00, low C-organic concentration (1.13 %),
low Cation Exchange Capacity (CEC) (10.21 me/100 g) and a very high mercury (Hg\(^{2+}\)) level of 574.17 ppm.

### 3.2. Compost chemical composition

Compost of *Tithonia diversifolia* had diverse chemical compositions (Table 1). C-organic concentration in *Tithonia diversifolia* compost was 39.97 %, N total 2.71 %. Based on those C and N concentrations, thereby the ratio C/N was 8.96. It seemed that N concentration in that compost was still above its critical value in order to allow mineralization. Therefore, it was expected that compost being used in this research would easily and readily undergo mineralization and would be able in releasing compounds in order to restore polluted soil. Soil pH value reflected the solubility of hydrogen ion in the soil and also depicted soil acidity level. Soil pH is highly influential on the dispersion activities of heavy metals in the soil and the absorption of nutrients in plants.

**Table 1. Compost chemical composition tithoniadiversifolia**

| Variable         | Value   |
|------------------|---------|
| pH H\(_2\)O      | 7.52    |
| pH KCl           | 6.94    |
| C - organic (%)  | 28.25   |
| N - total (%)    | 3.15    |
| P - total (%)    | 0.72    |
| K - total (%)    | 4.23    |
| Ca – total (%)   | 2.27    |
| Mg – total (%)   | 1.21    |
| Ratio C/N        | 8.96    |
| Humic Acid (%)   | 25.1    |
| Fulvic Acid (%)  | 5.41    |

### 3.3. The Impact of the provision of humic acid and fulvic acid of tithoniadiversifoliacompost on the change in soil hg-chelate(incubation experiment)

The highest concentration of Hg-chelate (141.52 ppm) was found in the treatment of HA125 on the 35th day, followed by treatments of HA100 (136.77 ppm), HA75 (86.43 ppm) and HA50 (81.68 ppm) (Fig. 1), respectively.

**Figure 1.** The Impact of the provision of humic acid *Tithonia* (HA) on the concentration change of Hg-chelate

The amount of Hg-chelate due to the humic acid provision was increased from 55.11 ppm (control) to 81.28 ppm, or up to 141.52 ppm were achieved from 5 until 40 days of incubation observation. In general, all treatments had led to the Hg-chelate concentration increased 1.5-2.5 times compared with the control ones.

The biggest change in Hg-chelate concentration due to fulvic acid provision was found in the treatment of FA125 (155.96 ppm) on the 40th day of observation and then followed by FA100 (150.98
ppm), FA75 (114.08 ppm) and FA50 (96.12 ppm), respectively. The amount of Hg-chelate was increased from 55.03 (control) to 94.63 ppm and to 155.95 ppm. Altogether, all treatments had led to an increased in Hg-chelate in 1.6-2.7 times than the control ones.

Figure 2. The Impact of the provision of fulvic acid \textit{Tithonia} (FA) on the change of Hg-chelate concentration

3.4. Discussion
The research results revealed that there was a real change in Hg concentration due to the humic acid and fulvic acid which indicated the role of humic acid and fulvic acid in binding the dissolved Hg for forming organo-metallic (chelate) bond in the soil thus increased the Hg-chelate concentration (Figure 1 and 2). The decreasing Hg solubility after being treated with humic acid was due to the form of complex-organo-metallic (Hg-chelate) compounds between that humic acid and Hg.

The concentrations of humic acid and fulvic acid in \textit{Tithonia diversifolia} compost are 25.10 % and 5.41 %, respectively. The concentration of both organic acids would affect the soil’s chemical properties. Organic acids like humic, fulvic, acetic, oxalic, butyric, lactic, and citric had high ability in chelating heavy metals, such as soil Hg \cite{9}. In order to solve the problem of polluted soil in the gold extraction area of Poboya, it’s better to use low technological input and \textit{in situ}. One of the alternatives for doing so could be achieved by using organic substances or compost. However, adding these organic substances/compost should carefully consider their chemical compositions \cite{10}.

The concentration of humic acid in \textit{Tithonia diversifolia} compost was 25.10 %, whereas the concentration of fulvic acid was 4.1 %. The concentration of those organic acids in that compost would have Impacted on the chemical properties of the soil, including the activities of Hg. Organic acids like humic, fulvic, acetic, oxalic, butyric, lactic, and citric had high ability in chelating heavy metals, such as soil Hg, which become not available for plants \cite{11}.

Fulvic acid treatment in the form of \textit{Tithonia diversifolia} compost extract exhibited that real Hg-chelate was better than humic acid. Other studies had demonstrated that the provision of fulvic acid was better than humic acid originated from organic substances of \textit{Tithonia diversifolia} on Ultisol and was able to increase Al-chelate 2-4 times in incubation for 90 days \cite{12}. The effect of fulvic acid and humic acid in increasing Hg-chelate was related to the organic acids produced by compost extract of \textit{Tithonia diversifolia}. The provision of humic acid and fulvic acid on the soil that had a high concentration of heavy metals would be able to lower the concentration of those metals \cite{8}. The decreasing concentration of Hg in the soil solution was closely related to the occurrence of Hg binding into organic-Hg in the soil or being called as Hg-chelate. Humic acid and fulvic acid also contain a number of microorganisms functioning in revamping organic compounds in the soil; thus, carbon substances will be released from the soil solubility that would produce other organic acids. Humic acid and fulvic acid were able to react with Hg in the soil solution \cite{13,14}.

Furthermore, it was stated that chelation by organic compounds was able to organize the
availability of metals in the soil, especially humic acid, and fulvic acid had the ability to adsorb metals [15]. It seemed that the reactivity of fulvic acid toward Hg was higher in comparison with humic acid. The reason was that fulvic acid contained bigger groups of carboxyl, phenolic, and total acidity than the humic acid [12]. The high total acidity in fulvic acid was closely connected to the higher level of carboxyl group than the one found in humic acid [16]. Those properties had generated greater ability owned by fulvic acid compared with humic acid in forming complexes with metal cations in the soil.

All cumulative treatments had led to Hg decrease >50% Hg up to the 40th day of incubation. It indicated that the role of humic acid and fulvic acid in lowering the Hg concentration in the soil solution was highly strong. As to the process of decline speed, which had been outlined above, the greater fulvic acid had lowered the soil Hg, compared with humic acid, due to the higher carboxyl group found in fulvic acid, thereby fulvic acid was stronger in forming complexes with metal cations in the soil [16].

4. Conclusion

The fulvic acid in *Tithonia diversifolia* had better effect in the change of Hg-chelate compared with the humic acid. The fulvic acid in *Tithonia diversifolia* was able to increase the highest Hg-chelate (96.58%), meanwhile, the provision of humic acid only increased Hg-chelate in the highest of 83.06% which was achieved during 40 days of incubation.

Reference

[1] Palanivel P, Susilawati K, Ahmed O H and Majid N. M. 2013. Compost and crude humic substances produced from selected wastes and their effects on Zea mays L. nutrient uptake and growth *Sci. World J.* 2013.

[2] Mindari W, Aini N, Kusuma Z and Syekhfani S. 2014. Effects of humic acid-based cation buffer on chemical characteristics of saline soil and growth of maize *J. Degrad. Min. Lands Manag.* 2 259–68.

[3] Kasifah K, Syekhfani S, Nuraini Y and Handayanto. 2014. Effects of application of groundnut biomass compost on uptake of phosphorus by maize grown on an Ultisol of South Sulawesi *J. Degrad. Min. Lands Manag.* 1 159–64.

[4] Carolin C F, Kumar P S, Saravanan A, Joshiba G J and Naushad M. 2017. Efficient techniques for the removal of toxic heavy metals from aquatic environment: A review *J. Environ. Chem. Eng.* 5 2782–99.

[5] Isrun M B-C, Wahyudi I, Hasanah U, Laude S, Inoue T and Kawakami T. 2018. Tithonia diversifolia Compost for Decreasing the Activity of Mercury in Soil *Sci. Technol.* 11 79–85.

[6] Miralles I, Piedra-Buena A, Almendros G, González-Vila F J and González-Pérez J A. 2015. Pyrolytic appraisal of the lignin signature in soil humic acids: assessment of its usefulness as carbon sequestration marker *J. Anal. Appl. Pyrolysis* 113 107–15.

[7] Rostami S and Azhdarpoor A. 2019. The application of plant growth regulators to improve phytoremediation of contaminated soils: A review *Chemosphere* 220 818–27.

[8] Tan K H. 2010. *Principles of soil chemistry* (CRC press).

[9] Zulfikah Z, Basir M and Isrun B. 2014. Konsentrasi merkuri (Hg) dalam tanah dan jaringan tanaman kangkung (Ipomoea Reptans) yang diberi bakoki kirinyu (Chromolaena Odorata L.) pada limbah tailing penambangan emas poboya kota palu *Agrotekbis* 2.

[10] Song C, Zhang Y, Xia X, Qi H, Li M, Pan H and Xi B. 2018. Effect of inoculation with a microbial consortium that degrades organic acids on the composting efficiency of food waste *Microb. Biotechnol.* 11 1124–36.

[11] Wu M, Song M, Liu M, Jiang C and Li Z. 2016. Fungicidal activities of soil humic/fulvic acids as related to their chemical structures in greenhouse vegetable fields with cultivation chronosequence *Sci. Rep.* 6 32858.

[12] Wahyudi I, Handayanto E, Syekhfani S and Utomo W H. 2010. Humic and Fulvic Acids of Gliricidia and Tithonia Composts for Aluminium Detoxification in an Ultisol *AGRIVITA, J.*
Agric. Sci. 32 216–24.

[13] Jiang J, Wang Y-P, Yu M, Cao N and Yan J. 2018. Soil organic matter is important for acid buffering and reducing aluminum leaching from acidic forest soils Chem. Geol. 501 86–94.

[14] Lima F R D, Martins G C, Silva A O, Vasques I C F, Engelhardt M M, Cândido G S, Pereira P, Reis R, Carvalho G S and Windmöller C C. 2019. Critical mercury concentration in tropical soils: Impact on plants and soil biological attributes Sci. Total Environ. 666 472–9.

[15] Piri M, Sepehr E and Rengel Z. 2019. Citric acid decreased and humic acid increased Zn sorption in soils Geoderma 341 39–45.

[16] Biester H and Zimmer H. 1998. Solubility and changes of mercury binding forms in contaminated soils after immobilization treatment Environ. Sci. Technol. 32 2755–62