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Effectivity of Humic Substance Extracted from Palm Oil Compost as Liquid Fertilizer and Heavy Metal Bioremediation

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Abstract

Humic substances extracted from compost materials were proven able to chelate heavy metals. While the waste from Palm oil as the source material of compost is increasing, consequently the humic substances production from palm oil waste is promising. On the other hand, agricultural lands that were treated with high input which caused heavy metal accumulation (pollutant) up to hazardous level also increasing. The aim of this research was to evaluate the effectiveness of humic substance extracted from Palm Oil compost as liquid fertilizer and bioremediation of copper (Cu). The experiment was designed to discover a product which effectively improved the characteristics of acid soils, bioremediation of heavy metals, and plants production. The results of the experiment revealed that the content of pure humic substance extracted from compost of Palm Oil empty bunches waste was very low, 2.01%. It also contained very low in N, P, and K, which were 0.01%, 0.02%, and 0,11% of N, P_2O_5, and K_2O respectively. The treatment of metal Cu as much as 300 mg $Cu(OH)_2.kg^{-1}$ into the media added with humic substance enriched with NPK (4.38; 8.24; and 9.24) showed non significant differences on some cucumber plant variables. NPK enrichments to humic substance showed significant differences on some agronomic variables than that of control. The length of plant treated with 3/3 NPK enrichment revealed the longest average of 564.2 cm, or increased by 38%. The highest fresh weight was obtained by 4/3 treatment followed by 2/3 rate of NPK enrichment. Whie the longest cucumber fruit was obtained by 3/3 rate. Total soil N was very low, consequently the NPK sorption by cucumber was very low. While soil P availability was high, however the NPK enrichment lowered the fresh cucumber fruit P content instead. The ratio of NPK nutrients in plant and in soil was higher if treated with Cu addition compared to that of control.

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Keywords: biofertilizer, bioremediation, humic substance, copper, cucumber

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1. Introduction

The previous research results indicated that humic substabces extracted from some compost materials were effectively and more rapidly improved soil chemical properties of marginal or acid soils. It could decrease exchangeable Al and increased soil P availability through chelating process (Winarso, *et al*, 2009a; 2010), therefore it could be an alternative to cope with problems of marginally acid soils in Indonesia, which covered almost 102.8 million ha (Puslitbangtanak, 2006). On the other hand, intensive agricultural lands were under harmful condition, due to high content of high heavy metals. Wang (2006), stated that more than 10% of cultivated lands were contaminated with Cd, As, Cr, and Pb, which caused production lost more than 10 million tons, and more than 12 million tons agriculture product per year became hazardous, which also caused economical lost at least 3 billion US dollars per year.

Heavy metals accumulation varied along with plant species, and generally higher on dicotyedoneael compared to monocotyledoneae plants (Taub and Goldberg, 1996). While, on the other hand, the potential agricultural/organical waste, especially from palm oil was very abundant, approximately 6 million tons empty bunches in 2004 (23% of total), excluding of wet decanter solid (4%), stem (6.5%), fiber (13.0%), and liquid waste (50%). Based on the data released by Ditjenbun (2006), within the last 20 years, the addition of Palm Oil Estate areas reached 5 million hectares, or increased by 837%.

Up to nowadays, the utilization of organic waste for soil was just as composting, without any added values, therefore its commercial value was low. Increasing commercial value of compost by extracting it to produce humic substabces was a very promising practice.

The humic substances extracted from compost could utilized as the raw material of biofertilizer and environmentally friendly bioremediation for heavy metals. In addition, humic substances have superior characteristics compared to that derived from mining (Leonardit) which has been marketed commercially, especially abroad (Winarso, *et al*., 2009b).

Humic substances originated from mining contained very high Na, approximately 5%., while Na is generally needed by plants in very small amount. In fact, if Na is continuously added to soil, would cause soil compacted and dispersed when wet, and became easily eroded.

The mass and cheap production of humic substances usually would harvest low concentration, and its characteristic was determined by the quality of its raw materials. Therefore, some efforts should be applied to activate its functional groups, such as through pH manipulation and adding synthetic organic substances rich in functional groups. In addition, enriching humic substances with nutrients is very useful and beneficial to improve its functions and purposes as soil conditioner, fertilizers, and as heavy metals bioremediation. The chelating capability of humic substances could improve their main function as bioremediation for heavy metal or other soil-environment pollutants

The aim of this research was to evaluate the effectiveness and the capability of humic substance extracted from Palm Oil bunches waste in improving cucumber (or other plants) production and in reducing soil Cu (heavy metals) content.

2. Materials and methods

This research was performed at the Faculty of Agriculture, the University of Jember, during year 2013 to 2014. The main material utilized in this research was humic substance extracted from paln oil waste, which then enriched by macro nutrients, N, P, and K. The amount of N, P, and K applied were based on the fertilizer recommendation for Cucumber and the treatments applied. The N, P, and K amount were: 4,38:8, 24:9,24 or 4,38% N; 8,24% P_2O_5; and 9,24% K_2O (Wichmann, 1992).

The humic substance was harvested from the solution originated from composting process of Palm Oil empty bunches. The composting process was undergoing naturally without any additional enhancing materials, but only water and plastic cover to maintain the moisture content.

Palm oil waste ustilized in the research was collected directly from the production process. The humic substances accumulated from the process contained: 4000 ppm C or approximately 2000 ppm humic substance (Stevenson, 1982). The other humic substance characteristics were presented in Table 1.

Table 1., showed that humic substance derived from Palm Oil waste contained N, P, and K low to very low, therefore it needed to be enriched to improved their functions to be used as liquid fertilizer.

The enrichment of humic substance as to be in line with the research treatments was conducted by adding 4000 ppm C; 2.71 kg Urea 46% N; 6.54 kg SP 36% P_2O_5; and 4.8 kg KCl 60% K_2O. The planting medium utilized was 8 kg of soil in each polybag. The plant indicator used was the Cucumber, which then planted at the field. Some plant and soil variables were then measured within and during 6 weeks.

The experimental design used for this research was Randomized Complete Block Design (RCBD) having two factors. The first factor was the rates of NPK enrichment materials per plant. Those were as follows: Control (No NPK enrichment), 1/3 of recommended rate (1/3 NPK: 3.3 gr Urea, 7.7 gr SP-36, and 5.7 gr KCl per plant); 2/3 of recommended rate (2/3 NPK: 6.7 gr Urea, 15.3 gr SP-36, and 11.3 gr KCl per plant); 3/3 of recommended rate (3/3 NPK: 10 gr Urea, 23 gr SP-36, and 17 gr KCl per plant); and 4/3 of recommended rate (4/3 NPK: 13.3 gr Urea, 30.7 gr SP-36, and 22.7 gr KCl per plant).

The second factor was the rates of Cu heavy metal ($Cu(OH)_2$), as follows: 0 (Control): 0 mg $Cu(OH)_2.kg^{-1}$ soil medium; and 1: 300 mg $Cu(OH)_2.kg^{-1}$ soil. The treatment combination of this experiment were replicated 3 times.

Table 1. Chemical Characteristics of humic substance extracted form Palm Oil Bunches Compost and Other Humic Substabces

Variable	Unit	**Palm Oil[1)]**	**Palm OIl[2)]**	Cassava	Rice Straw	Soybean	Humic K-Plus 26%[3)]
Humic Substances	%	**2,01**	**1,09**	-	1,13	-	63,6
Humic Acid	%	**1,57**	**0,9**	-	1,10	-	29,1
Fulvic Acid	%	**0,51**	**0,2**	-	0,30	-	34,5
Organic Acids::							
Acetate	ppm	**56**	-	46	94	39	-
Citrate	ppm	**18**	-	10	12	16	-
Oxsalate	ppm	**20**	-	16	17	22	-
Propionate	ppm	**2**	-	4	6	9	-
Butirate	ppm	**1**	-	Tt	1	Tt	-
Succinate	ppm	**21**	-	11	16	18	-
Fumarate	ppm	**9**	-	21	11	8	-
Ketoglutamate	ppm	**2**	-	tt	tt	1	-
pH		**8,60**	**5,50**	4,60	7,60	8,70	10,00
Organic-C	%	**0,32**	**0,12**	1,69	0,17	0,17	5,53
C/N		**23,2**	**8,1**	30,2	15,0	6,8	3,0
C/P		**37**	**14**	194	39	39	-
N	%	**0,01**	**0,01**	0,06	0,01	0,03	1,86
P_2O_5	%	**0,02**	**0,02**	0,02	0,01	0,01	0,00
Basic Cations:							
K_2O	%	**0,11**	**0,10**	0,06	0,06	0,10	29,19
NaO	%	**0,01**	**0,02**	0,02	0,01	0,02	4,66
CaO	%	**0,62**	**0,62**	0,68	0,49	0,92	1,23
MgO	%	**0,13**	**0,09**	0,31	0,13	0,13	0,13
Micro Nutrients and Heavy Metals							

Variable	Unit	**Palm Oil[1)]**	**Palm OIl[2)]**	Cassava	Rice Straw	Soybean	Humic K-Plus 26%[3)]
Fe	Ppm	**11,0**	**3,8**	68,3	1,3	6,0	9,8
Cu	Ppm	**t u**	**t u**	t u	t u	t u	t u
Zn	Ppm	**0,75**	**1,83**	9,00	2,38	3,50	6,75
Mn	Ppm	**298**	**1012**	295	679	834	1272
Mo	Ppm	**163**	**87**	101	71	121	81
Pb	Ppm	**0,43**	**t u**	t u	t u	1,00	9,00
B	Ppm	**305**	**203**	148	250	314	259
Al	Ppm	**1,58**	**1,58**	3,15	4,70	t u	3,53

- Not Analyzed; tt Not detected, [1)]Source of empty bunches; [2)]Source of waste process; [3)]Traded Products of Australian Industries (Winarso et al., 2009).

3. Results and discussion

3.1. Characteristics specific of humic substance extracted from palm oil compost

In general, the levels of N, P, and K macro nutrients of composted waste oil palm bunches were low and very high in C/N ratio. Palm oil waste in the form of empty bunches would take quite longer time to decompose compare to other plant waste such as soybean and rice plants waste. This is due to its very high C/N ratio, which is approximately 50 to 60. The results of Yunindanova (2009) research also revealed that crushed empty bunches Palm oil waste with C/N ratio about 41.8 took 10 weeks to decompose. Complete data empty bunches Palm oil waste decompositions were listed in Table 2. Decomposition process in this research was allowed undergone naturally to avoid additional nutrients from outside.

Table 2. Concentration of nutrients in palm oil bunches compost

Time Composting (weeks)	Nutrient									
	N %	P %	K %	Ca %	Mg %	Na ppm	C %	C/N	Fe %	Mn ppm
4	1,06	0,07	1,34	0,28	0,23	10,8	48,9	46,1	0,15	78,0
6	1,2	0,06	0,83	0,11	0,15	9,1	46,2	38,5	0,09	60,4
8	1,34	0,08	1,22	0,24	0,25	9,2	47,1	35,2	0,24	89,7
10	1,2	0,02	1,38	0,05	0,09	9,1	50,0	41,8	0,05	26,5

Time Composting (weeks)	Nutrient								
	B ppm	Cu ppm	Pb ppm	Cd Ppm	Hg Ppm	As ppm	pH H_2O	Ash %	Water %
4	8,4	19,5	tt	0,21	12,9	tt	8,21	6,14	70,23
6	8,7	15,8	tt	0,25	19,4	tt	8,66	7,04	71,13
8	10,7	24,8	tt	0,08	13	tt	8,58	9,81	67,68
10	7,7	12	tt	0,08	19,5	tt	7,89	6,07	67,41

Yunindanova (2009)

The chemical characteristics of humic substance extracted from (1) empty bunches Palm oil waste compost, and (2) Palm oil industrial waste, were listed in Table 1. It was showed that humic substance content for research materials was relatively low. That was due to that the humic substance extracted from Palm oil waste compost by gravitasion process. The Table 1. showed that humic substance in the research material was very low compared with humic substance commercially produced from mining (K-humic plus, 26%). However, was relatively equal with humic substance extracted from rice straw. The better chemical characteristic of humic substance of palm oil compost was low in Na content.

The NaO content of K-Humic plus 26% was 4.66%, while its content of Palm oil waste compost was 0.01%, and was 0.02% from Palm oil industrial waste. In stabilizing the high Na content usually was enriched by stabilizing cations such as K and Ca (K_2O and CaO). The K_2O content in commercial humic substance, K-Humic Plus 26% was 29.19%.

The organic acids content in humic substance extracted from Palm oil waste compost consisted of acetic acid (CH_3COOH, both aliphatic and single carbocilic), which was 56% of the total 56% of a total of 8 organic acids analized. All of that acids (Acetic, Fumaric, Cetogltamic, Succinic, Propionic, Butiric, Oxalic, and Citric acids) contained carbocilic functional groups (-COOH), both double and single bond (Hart *et al*., 2003). These functional group will dicosiate their protons (H^+), and produce negative charge acids or substances, which then will chelate Al or other metals in soil (Essington and Anderson, 2008).

The chemical characteristics of humic substance extracted form Palm oil bunches compost and other humic substabces showed in Table 1. indicated that humic substances extracted from compst of different sources (palm oil and rice straw) relatively have the same charecteristics except their quantity. Those data could improve the previous information which stated that the characteristics of humic substances significantly depending upon their source materilas. The differences of their variables were on their value. The humic substance of Palm oil empty bunches had pH 8.6 which higher than humic substances of rice straw with pH 7.6.

3.2. Agronomic variables of cucumber on treatment of Cu addition and rates nutrient (NPK) enrichment

Cucumber agronomic variables used to evaluate the treatment effect Cu addition and the addition of various concentrations of nutrients (NPK) enrichment on humic substances are: length of plant, number of leaves, fresh weight of fruit and length of fruit showed in Figure 1 to 4.

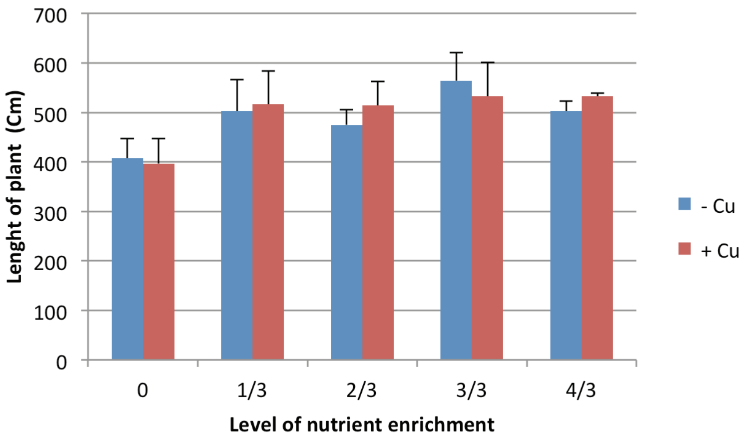

Figure 1. The cucumber length of plant on treatments of Cu addition and level of nutrient enrichment

Based on field measurements indicated that the length of the cucumber plants on the treatment of Cu addition and rate of nutrient enrichment are showed in Figure 1. The addition of Cu (300 mg $Cu(OH)_2.kg^{-1}$ soil) in several of humic compounds enriched nutrient doses were not significantly different (blue to red). However, the effect of nutrient enrichment on humic substances given to the growing media showed significantly different when compared with those not treated with an average of 407.4 cm (between images of the same color either blue or red).

Length of plant of the treatment 3/3 rate of nutrients (NPK) enrichment showed the greatest elongation of plants averaging 564.2 cm or up 38.5%.

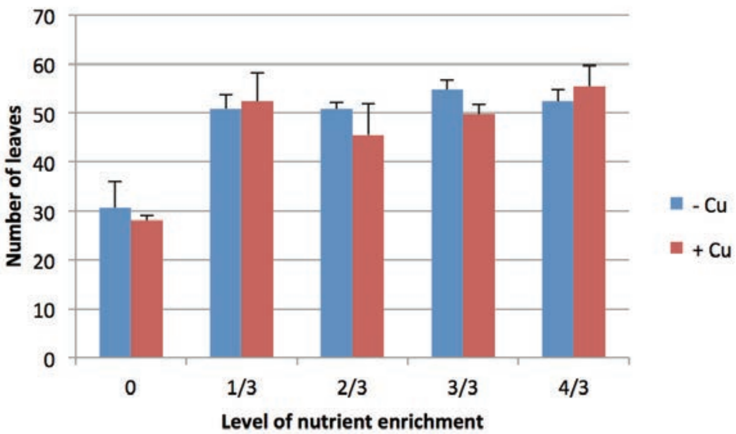

Figure 2. Number of cucumber leaves on treatments of Cu addition and level of nutrient enrichment

Increasing the length of the cucumber was followed by the number of leaves (Figure 2). The number of leaves in the rate 3/3 of nutrients (NPK) enrichment showed the greatest with an average of 82 cm or up 59% than control (no NPK enrichment). Level of nutrient enrichment 3/3 was the best effect on length plants and leaves number was not followed by the production of fresh weight of fruit cucumber. The highest fruit fresh weight on 4/3 level NPK enrichment and followed by 2/3. Completed result of the fresh weight of the fruit is showed in Figure 3. But after seen length the fruit (Figure 4), the highest in the treatment of 3/3, as well as on the length and number of leaves.

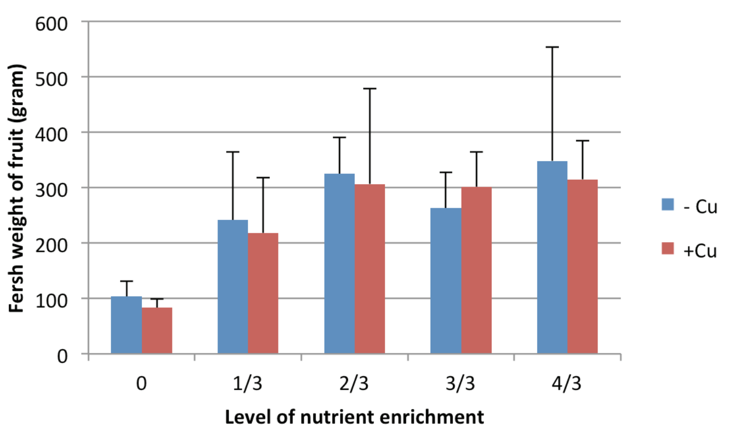

Figure 3. The fresh weight of cucumber fruit on treatments of Cu addition and level of nutrient enrichment

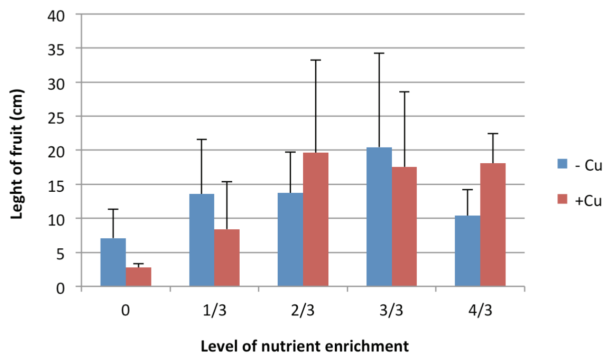

Figure 4. The length of fruit cucumber on treatments of Cu addition and level of nutrient enrichment

Evaluation of the use of water cucumber plants for 50 days of growth in 8 kg soil is showed in Figure 5. Based on Figure shows that the water needs to follow the pattern of cubic by the formula Y = -1,093x2 + 77,10x + 1034 (Y = crop water requirement in ml and x is the age of the plant in days). This water needs, especially just for transpiransi, because evaporation does not occur or can be ignored because pot cultivation covered with plastic.

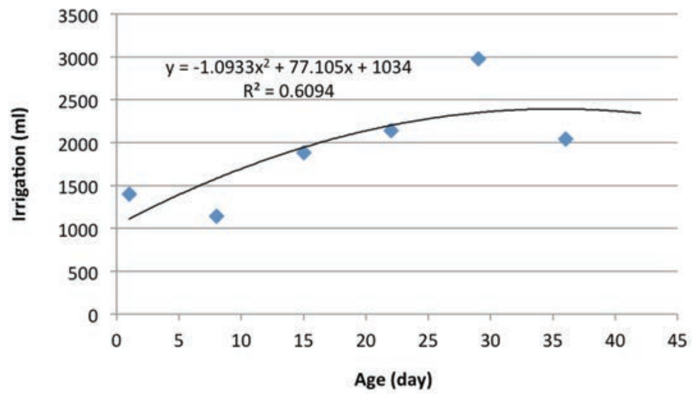

Figure 5. The use of water during cucumber growing on treatments of Cu addition and level of nutrient enrichment

3.3. Level nutrients NPK in soil and cucumber tissue and Cu in cucumber tissue

The treatment of nutrient enrichment in humic compounds extracted from palm oil compost combined with the addition of Cu does not significantly raise the level of N-total soil after harvest (Figure 6). Levels of N-total soil is approximately 150 mg $N.kg^{-1}$ or relatively very low. Hardjowigeno (1995) said hight levels of total soil is varies between 5,100 to 7,500 mg $N.kg^{-1}$. The condition or status of N soil is very low impact on content of N-tissue in the cucumber fruit low (Figure 7). Relationship or correlation N-total soil with N concentration in fruit tissue is low, r = 0.21 and the average ratio between N in tissue with soil around 10.2 N. It is mean content N in the tissue higher than in the soil. These ratio comparison showed the treatment of Cu addition is higher than is not treated with Cu. Figure 7 also showed that the addition of Cu in $Cu(OH)_2$ 300 $mg.kg^{-1}$ tend to increase the levels of N in tissue cucumber. Increased N in the fruit cucumber an average 304 mg $N.kg^{-1}$.

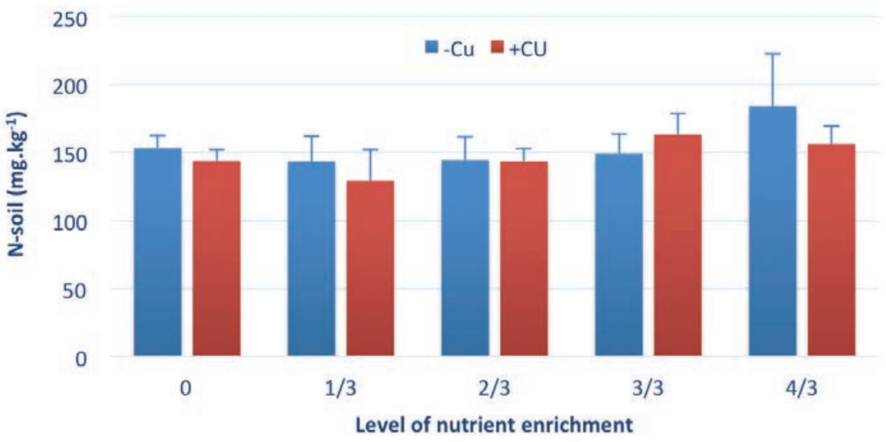

Figure 6. N-soil level at time of harvest on treatments of Cu addition and level of nutrient enrichment

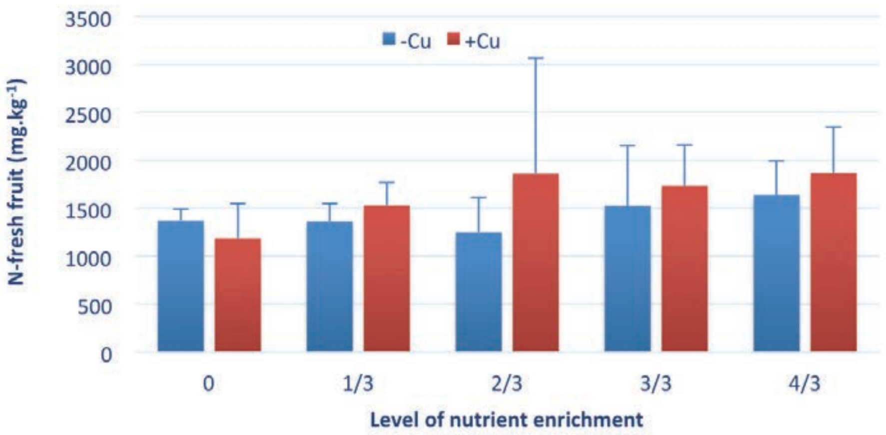

Figure 7. The N concentration of fresh cucumber fruit on treatmens of Cu addition and level of nutrient enrichment

By contrast with the level of N-total soil, the availability or content of P-available soil after harvest is very high and varies between 50 and 60 mg $P_2O_5.kg^{-1}$. Generally, said level of P-available is high varies between 26 to 35 mg $P_2O_5.kg^{-1}$. These high P-available in soil effected not significantly on the addition of humic substances enriched NPK. In addition, Figure 8 showed the addition of humic compounds enriched macro nutrients had lower levels of P in cucumber than not added. The amount of diminution was average 0.32 mg $P_2O_5.kg^{-1}$. It appears that this condition describe Leibig's law of the minimum and in this case that the limiting factor or the minimum condition is the level of N-total soil. The correlation between the P-available in the soil with P in tissue cucumber was 0.46 or moderate and the average ratio of P in the fruit tissue with the soil is around 1.28. The ratio P tissue: P soil showed the treatment of Cu addition is higher than is not treated with Cu.

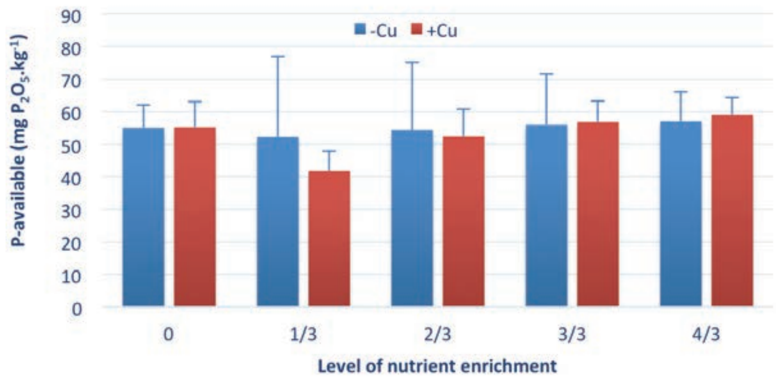

Figure 8. P-soil level at time of harvest on treatments of Cu addition and level of nutrient enrichment

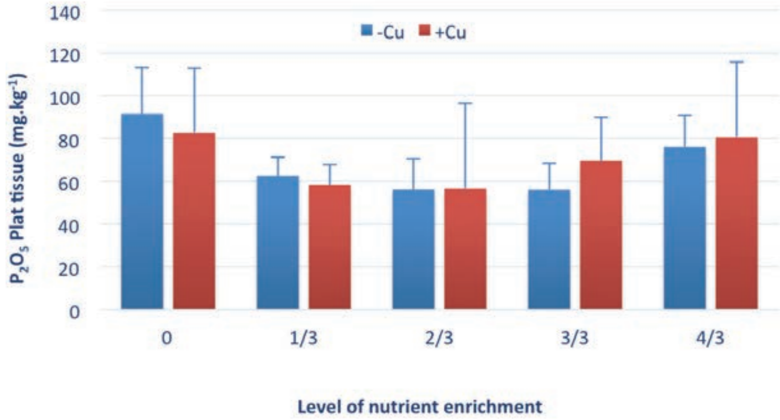

Figure 9. The P concentration of fresh cucumber fruit on treatments of Cu addition and level of nutrient enrichment

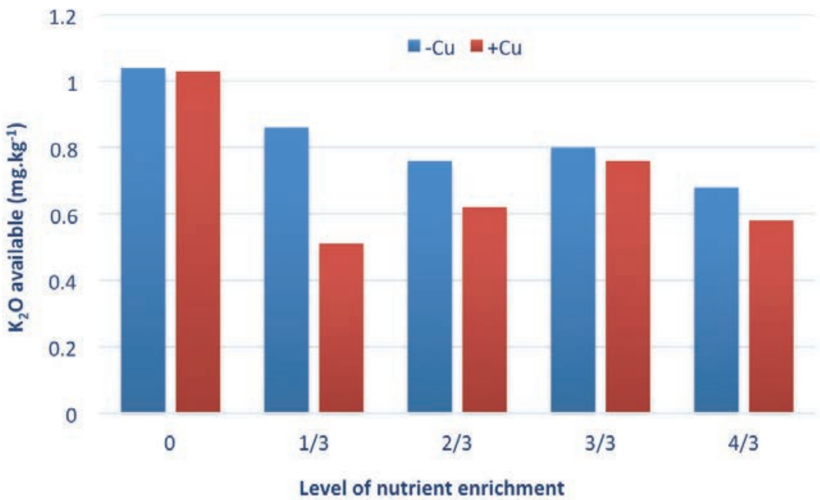

Figure 10. K-soil level at time of harvest on treatments of Cu addition and level of nutrient enrichment

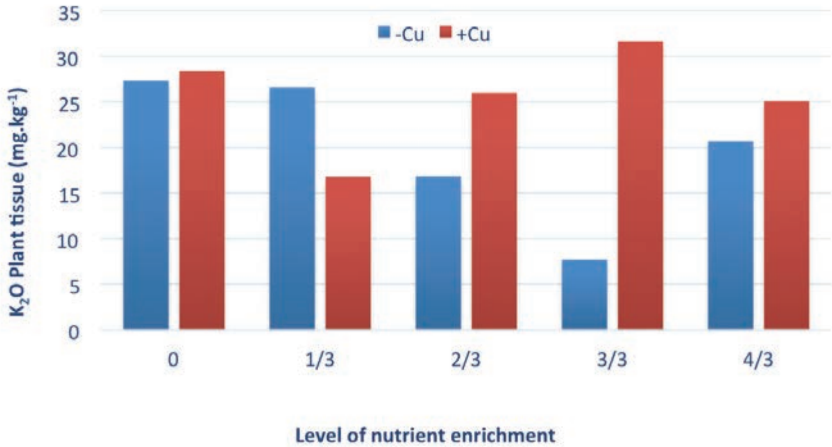

Figure 11. The K concentration of fresh cucumber fruit on treatments of Cu addition and level of nutrient enrichment

K-available soil after harvest high to very high, varying between 0.51 to 1.04 and an average of 0.76 mg $K_2O.kg^{-1}$ soil. Correlation K-available soil with K-tissue fruit was 0.29 or low. The ratio K tissue fruit : K soil around 27.93 with it's ratio the treatment of Cu addition is higher than is not treated with Cu

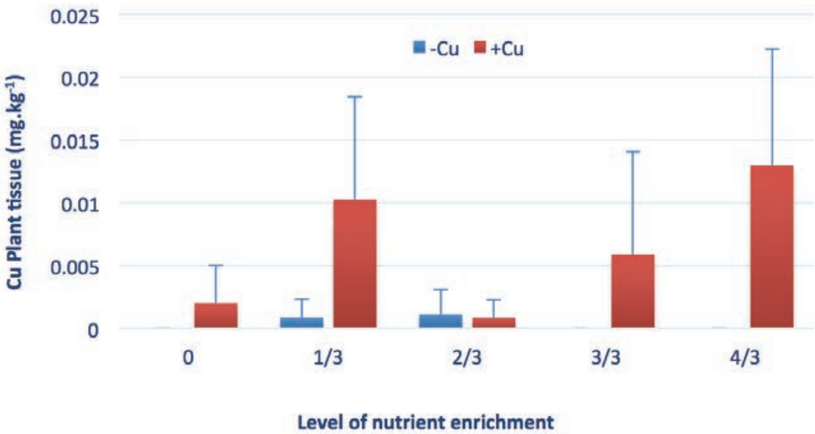

Figure 12. The Cu concentration of fresh cucumber fruit on treatments of Cu addition and level of nutrient enrichment

Addition of heavy metal Cu in the form $Cu(OH)_2$ in the growing media of cucumber shown to increase the levels of Cu in fruit cucumber. Figure 12 showed treatment of Cu significantly increase the uptake of Cu or the Cu content in the fruit cucumbers, particularly indicated in the treatment rates of nutrient enrichment 1/3, 3/3, and 4/3 to control. Concentrations of Cu in these tissue are still much smaller when compared with the results Moreira et al. (2011) in soils polluted weight Zn. The results showed Zn in tissue *Verbascum virgatum*, *Hypochoeris radicata*, *Phalaris arundinacea*, *Conyza bilbaoana*, *Paspalum urvillei* and *Aster squamatus* varies from 34 mg.kg^{-1} in the stems and leaves of up to 2,440 mg.kg^{-1} in the roots. Therefore, this condition when associated with the production of fruit showed that the addition of Cu at 300 mg.kg^{-1} did not affect significantly reduce the production of fruit (Figure 11). The interesting thing is also shown from the results of An et al. (2011) compared the five species of plants (tomatoes, corn, grocery greens, cabbage, and Japan herbs) on the uptake of heavy metal contaminants (Cd, Pb, Cr, Cu and Fe) indicate the tomatoes absorb most compared with other crops, khususya the metals Cd. Metal accumulation in these tomatoes will increase if the plants are planted in a mixture with other plant species.

4. Conclusions

Based on the discussion can be concluded as 1) Addition of Cu (300 mg $Cu(OH)_2.kg^{-1}$ soil) and humic compounds enriched rates of nutrients (NPK 4.38: 8.24: 9.24) were not significantly effect to the fruit cucumber production, 2) Humic compounds enriched 3/3 rates NPK showed the greatest treatment in contributing elongation of plants averaging 564.2 cm or up 38.5%, 3) Fresh weight of fruit cucumber is not effected the treatment humic compounds enriched rates of nutrients (NPK) and added Cu, 4) Levels of N-total soil is so low that NPK uptake cucumber is very low, whereas the levels of P-available soil is so high that treatment humic compounds enriched NPK had lower levels of P in the tissue of cucumber fruit, 5) The ratio NPK in tissue: in soil is larger in treated with the addition of Cu than not added.

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