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Effectiveness of rice husk biochar in controlling heavy metals at polluted paddy soil

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Abstract. Polluted irrigation can degrade soil chemical properties and then decrease land productivity. This research aimed to compare the effectiveness of biochar against manure in reducing the concentration of some heavy metals(HM) in the polluted rice field. This pot trial was conducted at Glasshouse using two types of amelioration (biochar and manure). Biochar and manure were incubated with paddy soil under field capacity at the glasshouse for one month. The results showed that increasing the dosage of either biochar or manure applied decreased the availability of HM, especially Fe (r=-0.87, r=-0.89) and Mn (r=-0.82, r=-0.91), respectively. However, there was no effect of biochar (r=0.25) but increased by manure (r=0.95) application on Zn concentration. Furthermore, some other heavy metals concentration also decreased, such as Ag (r=-0.89), Pb (r=-0.54), Cu (r=-0.51), Cr (=-0.50), and Ni (r=-0.64) by applying biochar but tended to increase by applying manure. Both biochar and manure could increase some plant nutrients, especially K (r=0.74, r=0.82), P (r=0.85, r=-0.44), Mg (r=0.98, r=0.91) and Ca (r=0.98, r=0.84), respectively.

1. Introduction

High heavy metal concentration becomes the main problem in the rice-field receiving polluted irrigation. The heavy metals could poison crop growth and decrease crop production. Some heavy metals mostly found in rice fields receiving irrigation from a gold mining area in Dharmasraya, West Sumatra Indonesia was Fe, Mn, Zn, Cr, Cu, Ni, and Pb [1].

Organic materials, especially manure, has been widely used as a soil ameliorant. It is cheap and easy to obtain by farmers. The ability of manure as organic material in chelating metals causes heavy metals polluting paddy soil to become inactive. It was reported that the application of 6% manure was able to immobile heavy metals (Cd, Pb, Zn) in contaminated soils [2].   The addition of manure significantly declined ($p<0.05$) the exchangeable and residual fractions of heavy metals in water [3] as well as Cd and Pb [4] in soil.

Furthermore, Yulnafatmawita [5] found that the addition of green manure as a source of organic matter and nutrient corn growth in Ultisols was able to increase water retention and aggregate stability of Ultisols Limau Manis. This because OM can bind water is much heavier than the dry weight itself. Besides, OM was also able to improve the distribution of pore size, so that the soil water holding capacity increased.

Another OC source that can be applied to control heavy metals contaminated soils is biochar. Biochar as a soil ameliorant has been informed lately about the function in retaining water so that it can improve the water availability of soils. Besides, organic materials and biochar are also able to reduce the bad effect of toxic elements on plant growth through the process of absorption; therefore, the solubility of the heavy metals becomes low, and they are not available to the plants. It was reported that the use of biochar and heavy metal tolerant bacteria was able to reduce the content of Zn, Mn, Cr, Cu, Pb, Ni, Cd plants by 1.78-9.23 times (with biochar) and 1.79-5.3 times (by bacteria) [6].

Furthermore, It was suggested that biochar either from waste or wood could increase the soil pH and reduce the availability of metal Cd, Pb, and Zn to plants [7] as found by de Figueiredo *et al.* [8] that the reduced solubility of heavy metals, for example, application of 15 t biochar/ha can decrease the concentration of Cd in soil to <1.2%, due to its high pH and pore volume, as well as its specific surface area.

Based on researches, both biochar and manure can reduce the availability of heavy metals in contaminated soils. However, it was not yet reported whether manure was more effective than biochar or not in controlling heavy metals in polluted soils.

2. Material And Method

2.1 Materials.

A pot trial was conducted in **laboratory** and glasshouse Agriculture Faculty Universitas Andalas Padang. The soil was taken from a polluted rice field in Dharmasraya, a rice production center in West Sumatra Indonesia [1]. The polluted soil was reclaimed using two types of amelioration, manure, and biochar. Manure used for this experiment was from cow manure collected from Padang city. The biochar was derived from rice husk.

2.2 Treatment.

This pot trial was conducted in two series, the first was for biochar, and the second one was for manure incubation. There are 6 different levels of biochar (0, 0.2, 0.4, 0.6, 0.8, and 1.0% C) and manure (0, 0.2, 0.4, 0.6, 0.8, and 1.0%C) applied which was based on the soil dry weight.

2.3 Preparation.

The bulk soil sample was taken from ricefield receiving irrigation from the Batang Hari River on which illegal gold mining took place in Sitiung, Dharmasraya, West Sumatra, Indonesia. The soil was sampled for 0-20 cm soil depth. The soil, then, was air-dried, ground, and then weighed. Soil water content was measure before weighing soil for treatments to find out the soil moisture correction (SMC).

$$SMC = 1 + \Theta w$$

SMC = soil moisture content correction

Θw = soil moisture content in weight basis (gg^{-1})

For each series of the experiment, the soil was weighed for a 2 kg oven-dry basis for each treatment unit. The soil was mixed with the biochar (the first series) and with manure (the second series)as the determined dosages. Then, the mixed materials (soil + ameliorant) were put into polybag and watered until field capacity, and then closely incubated for one month under glasshouse condition ($\pm 25^{o}$C temperature).

Following incubation, the soil was air-dried, and then measured the water content for soil moisture correction. The soil samples were then further ground for the heavy metals, SOM content, and some other properties. Soil OC content was analyzed using a wet oxidation method [9], then the SOM was calculated using the following formula:

$$\%SOM = \%SOC * 1.72$$

SOM = soil organic matter

SOC = soil organic carbon

Rice husk biochar was produced by using the soil pit method. Then, the biochar yielded was air-dried and then separated the unmatured parts. The water content of the biochar was also analyzed. Manure used was derived from cow dung mixed with the food residue. The manure used was considered mature, having the C/N ratio <10.

After being incubated for one month, the soil was analyzed the heavy metals by using X-Ray Fluorescence (XRF) PANalytical Epsilon 3. Then, the availability of 3 main heavy metals (Fe, Mn, Zn) in the polluted soil was analyzed using Atomic Absorption Spectroscopy (AAS).

The data collected was analyzed the variance at a 5% level of significance. Then, if there was a significant difference (F-test>F-table), the test was continued using HSD (Honestly Significance Difference) at a 5% level of significance.

Heavy metal adsorption percentage was calculated using the following equation [10].

$$\% \, Absorption = \frac{(c_o - c_e)}{c_o} \, x \, 100$$

where :

C_o (mg/L) was the initial concentration of heavy metal in solution

C_e (mg/L) was the final concentration of heavy metal in the solution,

3. Result & Discussion

3.1 Heavy Metal Availability in Soil after Biochar and Manure Application

Based on Figure 1, it was found that increasing biochar and manure applications decreased the availability of heavy metals, especially Fe and Mn, in paddy soils receiving polluted irrigation. Iron and Mangan significantly decreased as the biochar and manure application increased. As stated in Tabel 1, the application of biochar and manure significantly decreased the availability of heavy metals, especially Fe (R2= 0.761 and 0.797) and Mn, in polluted paddy soils. Biochar was able to reduce heavy metals mobility in soils [11]. However, at this research, Zn availability tended to increase by increasing biochar, but it was not significantly (R2= 0.06), while manure was significantly (R2=0.90). This result might be because manure contains some trace elements depending upon the source of the animal food. Therefore, the higher the dosage of manure applied is the more the concentration of trace elements in the soil.
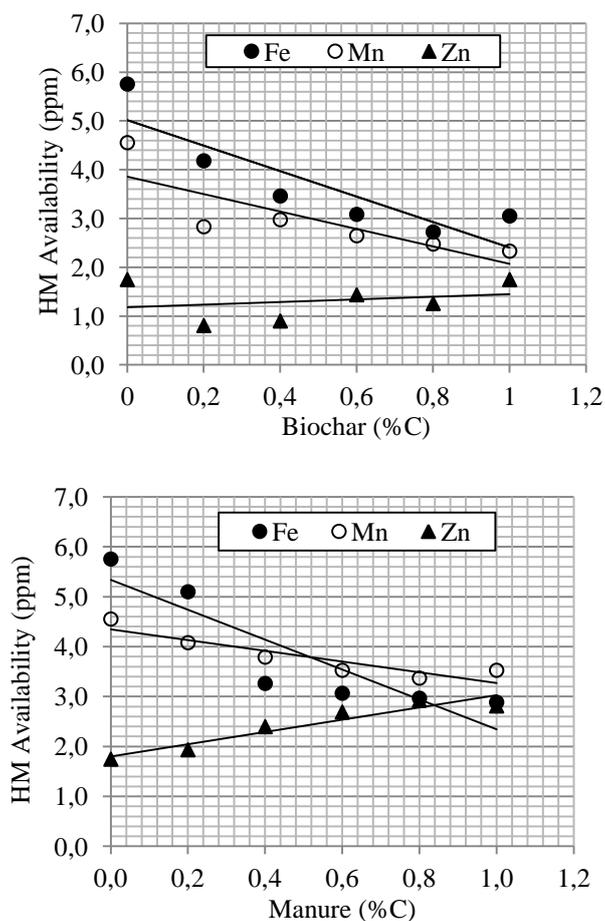
Figure 1. Effect of biochar and manure on heavy metals (Fe, Mn, Zn) availability in polluted paddy soil

Table 1. Regression equation between ameliorant applied and Fe, Mn, and Zn availability in polluted paddy soil

Ameliorant	Element	Regression Equation	R^2	r
Biochar				
	Fe	Y= -0.261X+5.013	0.761	-0.87
	Mn	Y=-1.787X+3.860	0.680	-0.82
	Zn	Y=0.271X+1.177	0.062	0.25
Manure				
	Fe	Y= -2.991X+5.334	0.797	-0.89
	Mn	Y= -1.075X+4.345	0.825	-0.91
	Zn	Y= 1.228X+1.803	0.900	0.95

Iron, manganese, and zinc are essential microelements for plant growth. Plants cannot grow normally without those elements; however, they were only needed in a small amount. Therefore, as the concentration of these elements increases above the concentration needed by plants in soils, the

plants will be poisonous. High iron concentration was also found under the recent rice field. Iron in that soils can be removed by time through intermittent irrigation.
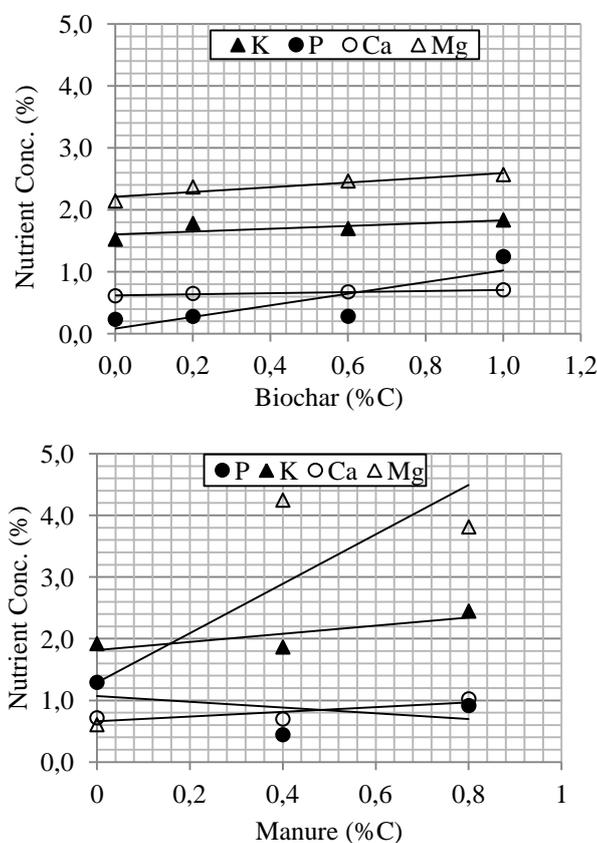

Figure 2. Effect of biochar and manure on nutrient concentration (K, P, Ca, Mg) in polluted paddy soil

Based on Figure 2, it was found that biochar and manure application increased the concentration of plant nutrients (P, K, Ca, Mg) in paddy soils. It means that rice husk biochar used still contained some plant nutrients. Manure is considered as organic fertilizer, contributing nutrients for plant growth. However, the increase in P concentration (R^2=0.196) was not significant under the manure application (Tabel 2). Phosphorus is a kind of plant nutrients in the form of an anion, which is easily fixed by Ca and Mg under high pH and by trace elements (especially Fe and Mn) under acid reaction (low pH). While under biochar application, the P element tended to increase (R2=0.98) as the biochar dosage increased significantly.

Tabel 2. Regression equation between ameliorant applied and plant nutrient (P, K, Ca, Mg) concentration in polluted paddy soil

Amelioran	Element	Regression Equation	R^2	r
BIOCHAR				
	K	Y= 0.224X+0.086	0.543	0.74

	P	Y= 0.090X+0.619	0.959	0.98
	Ca	Y= 0.937X+0.086	0.716	0.85
	Mg	Y=0.384X+2.211	0.873	0.93
MANURE				
	K	Y= 0.659X+1.815	0.673	0.82
	P	Y= 0.471X+1.073	0.196	0.44
	Ca	Y= 0.384X+0.660	0.701	0.84
	Mg	Y= 4.009X+1.286	0.650	0.81

Magnesium, as macro-essential elements for plant growth, sharply increased by increasing manure application. Plants need magnesium for stabilizing pH as Ca does, and for increasing photosynthesis activities in plants. On the other hand, Ca element in biochar ameliorated soil tended to be level of but still significant (R^2=0.716).

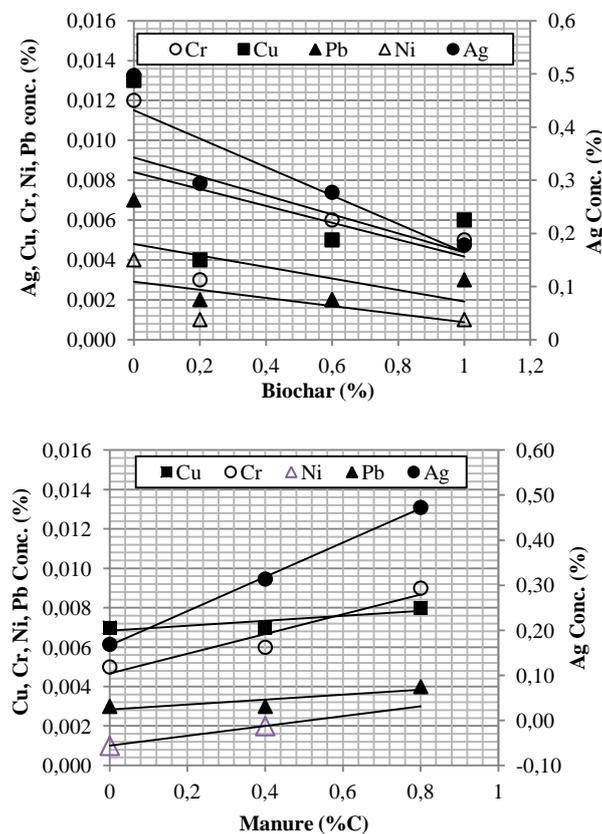Figure 3. Effect of biochar and manure on some trace element (Ag, Cu, Cr, Ni, Pb) concentration in polluted paddy soil

Based on Figure 3, there was a contrast effect between biochar and manure on the concentration of some trace elements in soils. Biochar application tended to decrease while manure tended to increase the trace elements (some heavy metals), especially Ag, Cu, Cr, Pb, and Ni (Tabel 3). The

concentration of Ag significantly decreases (R^2=0.785 with r =-0.88) as biochar applied increased, meanwhile it significantly increased (R^2=0.999 with r=-1.0) as the manure applied increased. It means that the application of manure must be first selected or identified the content; it can be dependent on the food they eat, or the characters of each animal producing it.

Tabel 3. Regression equation between amelioran on some trace element (Ag, Cu, Cr, Ni, Pb) concentration in polluted paddy soil

Amelioran	Element	Regression Equation	R^2	r
BIOCHAR				
	Ag	Y= -0.2673X+0.4318	0.7845	-0.88
	Cr	Y=-0.0042X+0.0084	0.2354	-0.49
	Cu	Y=-0.0047X+0.0091	0.2658	-0.52
	Pb	Y=-0.0029X+0.0048	0.2881	-0.54
	Ni	Y=-0.002X +0.0029	0.4068	-0.64
MANURE				
	Ag	Y= 0.38X+0.1667	0.9993	1.00
	Cr	Y=0.005X+0.0047	0.9231	0.96
	Cu	Y= 0.0013X+0.0068	0.7500	0.87
	Pb	Y= 0.0013X+0.0028	0.7500	0.87
	Ni	Y=0.0025X +0.001	1.0000	1.00

Table 4 presents the ability of soil ameliorant (biochar and manure) to reduce the availability or mobility of heavy metals, especially Fe, Mn, and Zn. Under biochar application, heavy metal absorption reached 64.39% for Fe and 48.84% for Mn at 1% dosage, while under manure application only reached 49.86% for Fe and 22.54% for Mn at 2% dosage.

Table 4. Bio-absorption of heavy metals by biochar and manure at polluted paddy soil

Ameliorant	Dosage	% Absorption		
	%C	Fe	Mn	Zn
Biochar	0.0	-	-	-
	0.2	27.35	37.86	54.04
	0.4	39.89	34.68	48.65
	0.6	46.44	41.91	17.82
	0.8	52.71	45.66	28.08
	1.0	64.39	48.84	0.00
	Average	46.15	41.79	29.72
Manure	0.0	-	-	-
	0.2	11.40	10.40	-37.31
	0.4	43.30	16.76	-54.10
	0.6	46.72	22.54	-67.62
	0.8	48.43	26.01	-61.09
	1.0	49.86	22.54	-59.89
	Average	39.94	19.65	-56.00

K-Malina [12] found that brown coal material gave the best amendment to reduce HM (especially Cd, Pb, Zn) mobility in soil and decreased the concentration in plants being tested. Organic matter can release and also hold some heavy metals in the soil [13]. The most important role of OM in reducing HM mobility is due to its high CEC and chelation process [14].

Table 5. Effectiveness of biochar in reducing heavy metals availability in polluted paddy soil

Dosage (%C)	Effectiveness of Biochar against Manure		
	Fe	Mn	Zn
0.0	-	-	-
0.2	2.40	3.64	-1.45
0.4	0.92	2.07	-0.90
0.6	0.99	1.86	-0.26
0.8	1.09	1.76	-0.46
1.0	1.29	2.17	0.00
Average	1.34	2.30	-0.61

Table 5 showed that the effectiveness of biochar in absorbing heavy metals in soil was higher than manure. Biochar was able to absorb Fe by 134% and Mn by 230% than that by manure. This result could be due to the structure of biochar having many pores that could absorb the heavy metals.

4. Conclusion

This study conclude that the availability of Fe and Mn decreased, but Zn tended to increase by increasing biochar and manure dosages applied. Heavy metals absorption by biochar (46.15, 41.79, 29.72%) > by manure (39.99, 19.65, -56%). The effectiveness of biochar against manure was equal to 1.34 (Fe), 2.30 (Mn), -0.61 (Zn).

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