Rice Straw Compost as Amendment to Reduce Soil Copper Toxicity in Lowland Rice Paddy Field

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A rice paddy field experiment was conducted during the 2012 dry season in Brgy. Cabiten, Mankayan, Benguet to test the efficacy of rice straw compost amendment in reducing available Cu in soil and observe its effect on rice yield. Three treatments in randomized complete block design were made with four replicates each: T_0 – no compost added, T_1 - compost applied at 16 kg m^{-2} and T_2 – compost applied at 32 kg m^{-2}. Mineral fertilizer was applied in all treatments. The subject of the study was the cold-tolerant rice variety, C18. Compost application significantly increased mean grain yield by 23.0% compared to control. The mean grain yield with treatment T_0 was 246 kg m^{-2}, with T_1 was 320 kg m^{-2} and with T_2 was 325 kg m^{-2}. The available mean soil Cu was significantly reduced from 281 ppm in the control to 25 ppm with T_1 and 15 ppm with T_2. The mean soil pH after harvest also significantly improved to pH 5.66 with T_0, to 5.95 with T_1 and to 6.12 with T_2. There was a significant correlation of the Cu contents in the soil and in rice roots with T_0 having the highest content in both soil and roots, decreasing with T_1 and lowest with T_2. Mean Cu contents in straws were very low at 3 to 5 ppm, and were not significantly different with all treatments. Roots contained significantly higher Cu (260 ppm with T_0, 155 ppm with T_1 and 26 ppm with T_2) than the straws. The results of this field study demonstrate that the use of rice-straw compost is a good remediation strategy for reducing soil Cu toxicity to the normal limit of 30 ppm, and for improving rice yield.

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INTRODUCTION

The Philippines, like the rest of Southeast Asia, Australia and the western Pacific, is rich in non-fuel mineral resources due to the various geologic processes that are happening in the region for the last 15 million years (Peters and Back 2003). For several decades, our country has ranked no. 4 in the world in gold production (Mitchell and Leach 1991).

Mining activities to extract the minerals have both positive and negative impacts on the country's economy and environment. Foreign investment in large-scale mining operations is one of the sources of foreign exchange of the Philippine government. The government also derives revenues from the sale of the products of mining activities. Mining also provides employment in rural communities. Moreover, it stimulates economic activities within the mine sites of operation. Mining companies also provide some other benefits such as school buildings, scholarships, hospitals and the like in the host communities. Mining, too, supplies minerals and metals that are essential components of equipment and gadgets especially in the electronic industry. On the other hand, the down sides of mining activities, *e.g.*, environmental destruction and degradation, are long-term and the communities in mine sites are the main sufferers. Mine tailings, the most important mine waste, are causing an array of environmental problems (Cooke and Johnson 2002, Li et al. 2008).

Mankayan, Benguet is the host municipality of an old mining company that has been in operation since 1936. In 1986, the dam of the tailing pond that impounded mine wastes was

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breached so that mine tailings overflowed and huge amounts of Cu-contaminated mine wastes carried by the Comillas River (referred to by the locals as the Mankayan/Lepanto River) inundated productive lowland rice paddy fields along the river bank in two barangays of Mankayan and three barangays of Cervantes, Ilocos Sur. The paddies now have a Cu content much higher than 30 ppm, the normal level of Cu in uncontaminated soil (Pfeiffer et al. 1988). The contamination of the agricultural fields led to lost, or greatly lowered, soil productivity. The paddies with presumably very high copper content were abandoned since rice plants could not grow on them right after the accident. At present, these highly contaminated areas (present level of available soil Cu > 220 ppm, possibly higher right after the accident) are covered with grasses and herbaceous dicots that established through the natural regeneration process, and are now used as areas for pasture. No research work has been done to address the problem of Cu contamination of these rice fields until this study and no official record exists. Hence, we do not have benchmark information on rice yield before and after the accident. Our 2013 wet season cropping data (Cuevas et al. 2014) show that rice yield depends on the level of available Cu in the soil and soil pH of the particular paddy we had studied. We found that a field with 359 ppm available Cu and soil pH of 7.0 had a yield of 0.067 kg m^{-2}, while a field with available Cu of 47 ppm and soil pH of 5.9 had a yield of 0.484 kg m^{-2}, using the same rice variety and cultivated in the same season of cropping.

Organic fertilizer or compost is a good form of fertilizer for damaged and marginal lands. Its importance does not rest only in supplying nutrients to the crops but also for the capability of organic matter (OM) of improving the physical and chemical properties of the soil, and OM's ability to chelate heavy metals and other pollutants.

Earlier, Cuevas (2009) demonstrated in a greenhouse experiment that *Jatropha* seedlings had much faster and luxuriant growth in marginal, acidic grassland soil amended with 16% compost from biowastes. The compost amendment significantly improved cation exchange capacity, water holding capacity and soil pH. Further, Gylienė and Višniakova (2008) showed that the complexation of heavy metals with natural organic matter is the most important reaction controlling the latter's transport in the environment and their bioavailability. Kumpiene et al. (2007) showed that organic matter had the most varying impact on the mobility of heavy metals. They found that the ability of OM to retain the element depends on several factors, such as soil pH, the degree of OM humification and the dominance of low solubility of high-molecular weight organic acids versus highly soluble low-molecular weight acids. van Herwijnen et al. (2007) showed that composts can increase or decrease the bioavailability of metals in soil. They found that these effects of compost amendment depend on the type of compost, the soil type and related contaminant levels, and that metal immobilization and bioavailability are governed by the formation of complexes between the metals and organic matter. O'Dell et al. (2007) reported that yard waste compost amendment in mine-contaminated soil grown with *Bromus carinatus* had exceptionally high Cu- and Zn-binding capacities that were attributed to high compost humic and fulvic acid concentrations. And Fontanilla and Cuevas (2010) demonstrated in a green house experiment that *Jatropha curcas* seedlings grown in potting medium consisting of 20% market waste compost mixed with high Cu (212 ppm) contaminated soil from Mogpog, Marinduque had reduced the Cu content to a normal level of 28 ppm Cu in six months of growth.

The present study was conducted to test if rice straw compost amendment can effectively reduce soil Cu toxicity and to observe its effect on rice yield. Several studies on the effect of organic amendments in rice paddy systems with high levels of heavy metals, *i.e.*, Cu and Cd, had been done in Southern China, but none had discussed the direct use of rice straw compost as amendment to reduce the level of available soil Cu, although Li et al. (2007) concluded that pig manure amendment has effectively reduced Cu content in rice grains. In the Philippines, this is the first study on the use of rice straw compost as amendment to reduce the level of available soil Cu in rice paddy systems.

Figure 1 A. Map of the Philippines showing the location of Benguet province (from Wikipedia.com)

Figure 1 B. Aerial photo showing the active tailings pond of the Lepanto Consolidated Mining Corporation in the municipality of Mankayan, Benguet

(Source: "Mankayan, Benguet" 16°53'34.82" N and 120°46'4.99" E. www.google.com/earth/connect)

MATERIALS AND METHODS

The study was conducted in Brgy. Cabiten, Mankayan, Benguet during the 2012 (January-April) season in a rice paddy field about 200 m from an active tailing pond of a large-scale mining operation. The soil texture of the rice field at the upper 15 cm is sandy silt turning into sandy clay below the 15 cm. Figures 1 A and B show the location of the research site.

Three treatments were made in a completely randomized block design with four replicates each:

T_0 – no compost added; mineral fertilizer applied
T_1 – compost applied at 16 kg m^{-2} + mineral fertilizer
T_2 – compost applied at 32 kg m^{-2} + mineral fertilizer

The mineral fertilizer was applied to each of the block replicates at the recommended rate based on soil chemical analysis. The rate of compost application was based on the findings of Cuevas (2009) that 16% compost mixed with acidic grassland soil significantly improved soil physical and chemical properties. Using the standard value of 2 x 10^6 kg ha^{-1} plow layer of soil, 16% compost is equivalent to 32 kg m^{-2} and its half dose is

Table 1. Results of the chemical analysis of rice paddy soil and compost used in the study

Parameters	Soil before treatment	Compost
pH	5.9	7.0
% OM	3.22	51.37
% Total N	0.16	2.24
P2O5 (ppm)	28.00	1.27
K2O (me/100g)	0.15	1.41
Cu (ppm)	281	

Note: Compost was not analyzed for Cu content since our data from another study showed that rice straws harvested in fields with Cu contamination had only 11 ppm Cu content. Schulte and Kelling (1999) stated that the normal level in plant tissues is 10 to 20 ppm. Therefore we did not analyze the compost from rice straw considering that the level of Cu is within the normal range.

equivalent to 16 kg m^{-2}. Compost was applied in a 3 m X 3 m plot at the middle of the rice paddy in each block replicate. All data were collected in a 2 m^2 subplot within the treatment plots. Each treatment plot measured about 84 m^2.

A cold-tolerant rice variety, C18, recommended by the Mankayan Municipal Agriculture Office, was planted. Rice straw compost was prepared *in situ* using 80% rice straw and 20% animal manure as substrate employing the static pile method. After a one-month incubation, when the substrates were no longer recognizable, the compost was considered ripe and was analyzed for % total carbon, % total N, % P as P_2O_5 and % K as K_2O. Paddy soil was also analyzed at the start of the field preparation for % OM, % N, available P (ppm), exchangeable K cmol($^+$)/kg and Cu contents. The results of these analyses are presented in Table 1.

At harvest time, rice straws from the treatment subplots were cut at the base close to the ground. Before threshing, the number of productive tillers was counted and shoot length was measured separately for each treatment. The roots were dug from the soil up to 30 cm deep and length was measured separately for each treatment. Rice grains were separated from the stalks and filled from empty grains. All plant parts were first air-dried and then oven-dried at 70^0C for 4 days and dry weights taken. The rice plant roots and straws from the treatment subplots were analyzed for total Cu content. Soil samples from the treatment subplots were taken, air-dried, pulverized and analyzed for available Cu content. The pH was also measured from the soil samples.

The data were subjected to t-test and Pearson correlation for statistical analysis. Reduction in Cu toxicity was assessed by comparing the means of the available soil Cu in the various treatments for significant differences. A conclusion, that a reduction had happened, was made if the treated plot means fell within the range of the normal levels of available Cu in the soil of $\leq$ 30 ppm (Pfeiffer et al. 1988). The means of the soil pH of the samples, which had been subjected to different treatments, were compared for significant differences and were correlated with the means of the available soil Cu in the various treatments. The dry weight of filled grains was used to evaluate rice yield. The means of the dry weights of filled grains, roots and straws, the number of productive tillers and root and shoot lengths, as well as the means of the Cu contents of rice roots and straws for the various treatments, were compared for significant differences. The amounts of compost applied were correlated with soil pH and levels of available soil Cu.

All Cu analyses of soil and plant tissue samples were analyzed by the Flame Atomic Absorption Spectrophotometry method at the Natural Science Research Unit of St. Louis University, Baguio City. Soil fertility analyses were conducted based on the method of Recel and Labre (1988) at the Soil Analytical Chemistry Laboratory, Agricultural Systems Cluster, College of Agriculture, University of the Philippines Los Baños (UPLB).

Table 2. Dry weights of shoots and rice grains in subplots with and without compost amendments.

Treatments	Shoot dry weight (kg m^{-2})	Grain (kg m^{-2})
T_O – Control; no compost	247.0 b	246.0 b
T_1 – 16 kg m^{-2} compost	301.0 a	320.0 a
T_2 – 32 kg m^{-2} compost	313.0 a	325.0 a

Numbers are means of 4 replicates. In a column, means with same letters were significantly different from the control at 10% level of significance by t-test.

RESULTS AND DISCUSSION

Table 2 shows the dry weights of the rice straws and grains taken from the treated subplots. Table 3 presents the data on selected growth parameters such as the number of productive tillers and shoot height and length of extracted roots after harvest. The mean grain yield and the mean dry weight of straws in compost-treated subplots (T_1 and T_2) were significantly different (at 10% level of significance) from those in the untreated subplot (T_0 - control). There was no significant difference between the compost-treated subplots; their means were almost equal (Table 2). The grain yield was found to have a slight positive correlation (at 10% level of significance) with compost application (r = 0.63, p = 0.067). The amount of compost applied was negatively correlated with available Cu in the soil (r = 0.70, p = 0.04), which indicated that when more compost was applied a significant reduction of Cu in the soil resulted. Thus it can be deduced that the increase in grain yield and mean straw dry weights was due to the reduction of Cu toxicity with compost application.

However, the rice crop in all treatments had heavy disease incidence of brown spot caused by the fungal pathogen *Bipolaris oryzae* (Figure 2). In this particular study, no attempt was made to quantify the difference in disease severity among the different treatments.

Figure 2. Rice plants growing in Cu-contaminated paddy field in Brgy. Cabiten, Mankayan, Benguet heavily infected by brown spot disease caused by *Bipolaris oryzae.*

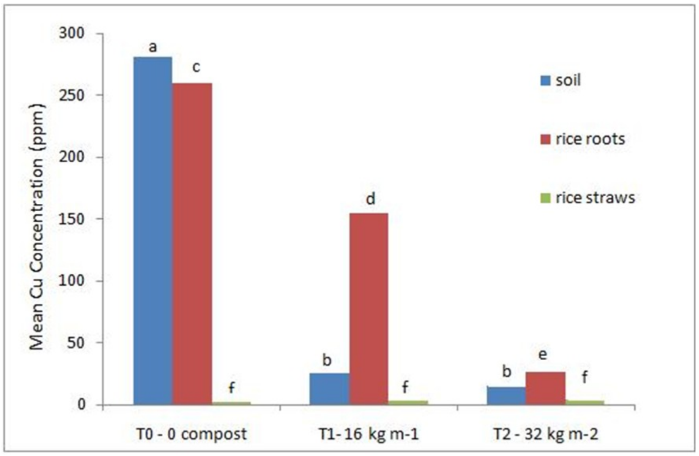

Figure 3. Comparison of Cu contents of soil, rice tissues after rice cropping in the treated subplots. Means with the same letter are not significantly different from each other at 5% level of significance.

Table 4. Mean soil pH of rice paddy soil after rice cropping

Treatment	Soil pH after harvest
T_O – Control; no compost applied	5.66 a
T_1 – 16 kg m^{-2} compost	5.95 b
T_2 – 32 kg m^{-2} compost	6.12 b

Numbers were means of 3 replicates; means with the same letter are not significantly different from each other at 5% level of significance.

Figure 3 presents the comparison of Cu contents of soil, rice roots and straws analyzed from samples taken from the different treatment subplots after harvest. Soil Cu content in T_0 was 281 ppm and was significantly reduced in compost-treated subplots: 25 ppm in T_1 and 15 ppm in T_2. No significant difference was noted between T_1 and T_2. The mean Cu content in rice roots was least in T_2 at 26 ppm, higher in T_1 at 155 ppm and highest in T_0 at 250 ppm; the differences were statistically significant. The Cu content of roots is slightly correlated with available Cu in soil ($r = 0.63$, $p = 0.07$). There was a highly significant negative correlation of the amount of compost applied with the Cu content of roots ($r = -0.99$, $p < 0.001$). Baker and Senef (1995) had found that the average Cu content in plant tissues is 10 mg g^{-1} dry wt, while Schulte and Kelling (1999) showed that Cu at > 50 ppm is to be considered an excessive amount in plant tissues. The data we gathered show that rice plants growing in soil with high available Cu do accumulate toxic levels of the element.

Studies on rice uptake of Cu and the changes in its levels in the rice tissues at various amendments were mostly in straw and grain (Xu et al. 2006, LI et al. 2008, Yu-Ping et al. 2006), and not in rice roots. They found that the concentration of Cu in straws and grain are related to the concentration of available Cu in the soil, which in turn was affected by the type of amendment done. However, Xu et al. (2006) mentioned that rice roots are more sensitive to Cu toxicity than other parts of the rice plant at relatively lower soil Cu levels (less than 300–500 ppm), but that the growth of the whole rice plant was severely inhibited at high soil Cu levels (300 to 500 ppm). They observed that the root weight reduction was dependent on the available soil Cu concentration and that the reduction is much larger in roots than in shoots with increasing available soil Cu levels. In our study, the mean Cu concentration in rice straws was very low in all treatments (3 to 5 ppm) and was significantly lower compared to the Cu content in roots. Our findings are similar to those of Li et al. (2008) that showed a significant linear correlation between the concentrations of available Cu and Cd in soils and the concentrations of Cu and Cd in rice straws and grain.

Table 4 presents the mean soil pH in the treated subplots after rice cropping. The highest mean soil pH was recorded in T_2 at 6.12, the lowest in T_0 at 5.40 and at the mid level in T_1 at 5.95. Soil pH is negatively correlated with soil Cu concentration ($r = -0.87$, $p = 0.025$), indicating that the lower the pH, the higher the available soil Cu.

Copper is an essential nutrient for plant growth needed in minute quantities. It is largely absorbed in the form of Cu^{+2} and is directly involved in photosynthesis as a component of the co-factor plastocyanin in the photosynthetic electron transport phase. It is also part of proteins and complexes and can bind with chromosomes to maintain their normal structure, and is an indispensable component of oxidative enzymes. However, toxic levels (> 50 ppm) (Schulte and Kelling 1999) reduce plant growth, act strongly on chromatin structures, and affect the photosynthetic apparatus and the senescence process (Maksymiec 1997). In rice, Xu et al. (2006) reported that increasing soil Cu concentration causes an exponential decrease in grain yield. The root dry weight, straw dry weight and grain yield decreased by 10% compared to the control with Cu concentration of 100 ppm; half of the biomass and grain yield was lost at 300 to 500 ppm Cu concentration. The findings of Zeng et al. (2011) in their study of the rice uptake of heavy metals showed that heavy metal concentrations in rice straw and grains were negatively correlated with soil pH value, but positively correlated with soil organic matter.

Yu-Ping et al. (2006) in their experiment on the uptake of Cu by different rice cultivars reported the effect of Cu (100 mg kg^{-1}) on rice growth and grain yield. They found that the accumulation of Cu in brown rice varied greatly in different cultivars. They stated that the process of Cu uptake from soils by roots is strongly governed by plant factors. Cu could be translocated from the roots to the above ground vegetative plant parts, leaves and stalks, and least to the grains, and there was a direct translocation from the Cu storage in the roots to grains with an intermediate Cu storage in the upper leaves. They hypothesized that the translocation of Cu from root to grain in the rice plant would be inhibited by all the organs on its pathway.

In our present study with compost amendment we got only 23% increase in grain yield over the control, even though the available Cu in the soil was reduced to the normal level of 30 ppm (Pfeiffer et al. 1988). This lower increase may be due to the brown spot disease incidence caused by *Bipolaris oryzae*. Brown spot is the most important disease in rice (Ou 1985) and had caused grain yield reduction of 50 to 90% during the Bengal famine in 1942 (Woodhead and Famine Inquiry Commission India 1945). The disease is associated only with abnormal or poor soil, *i.e*. in areas with high Cu content. Copper interferes with the absorption of silicon. Silica deposits in rice leaf cuticle creates a physical barrier that gives the plant general resistance to the entry of leaf pathogens (Dallagnol et al. 2011). At toxic Cu levels in the soil, less silicon is absorbed by the rice plants making them highly susceptible to brown spot disease. In this study the rice plants were already affected at the early stage of plant growth and this may have affected grain yield. The source of seeds sown by the farmer greatly affected the rate of infection, as well as the stage of growth of the rice plants when the infection occurred. The pathogen is seed-borne (IRRI Fact Sheets 2007) and the farmer of the plot in our study had used the seeds of the previous cropping from the same field, so that at the very early stage of seed germination and seedling establishment the rice plants in all treatments were already and equally diseased. The positive effect of compost application on available Cu reduction probably did not have any more effect on seedlings already infected. In as much as we did not monitor disease progression, we cannot present data on the effect of compost application on brown spot disease suppression.

A follow-up study of the interactions of brown spot disease incidence, available soil Cu and amount of rice straw compost amendment applied, and of the available soil Cu and silica content of rice plant tissues has been assigned as a Master of Science Plant Pathology graduate research topic so that a greater understanding of the effect of Cu could be obtained. Preliminary experiments conducted by the UPLB Plant Pathology graduate student on the effect of compost application on brown spot disease suppression in a nearby field has demonstrated that there is a significant negative correlation between the rate of compost application and brown spot disease incidence. In that study, the seeds sown in the field were taken from Pangasinan where there is no incidence of brown spot disease and, therefore, did not carry the spores of the pathogen (Malamnao, personal communication).

In our study, we have clearly demonstrated that rice straw compost amendment resulted in a decrease in the available Cu in the soil and, consequently, a significantly higher grain yield was achieved in compost-treated subplots. We also showed that soil-available Cu is inversely correlated with the soil pH of the subplots.

The same trend had been reported by O'dell et al. (2007) who found that maximum plant biomass of *Bromus carinatus* was achieved in Cu-Zn mine-spoil potting medium when amended with compost and fertilizer in combination. They commented that pH is often the main factor determining the plant-availability of the metals, with availability being greater at lower soil pH. Humic substances, major constituents of the OM of compost, can form stable metal chelates and reduce Cu availability. Li et al. (2008) pointed out the significant influence of soil pH on the availability of Cu and Cd and the uptake of the metals by rice plants in pot experiments utilizing several amendments in contaminated soil; highest grain yield was observed on treatments with limestone that increased soil pH significantly. Zeng et al. (2011) in their study had similar findings that heavy metals are less available at higher soil pH. They further proposed that organic matter has a dual role in the availability of heavy metal in soil, *i.e*., that humic substances in organic matter form stable complexes that reduce availability and mobility of heavy metals in soils, but that organic matter can also supply organic chemicals to the soil solution, which may serve as chelates and increase metal availability to plants.

Our study showed that rice roots accumulation of Cu is directly related to the soil Cu concentration - the higher the available Cu in soil, the higher the amount of Cu accumulated by the rice roots. There was a minimal amount of Cu present in rice straws (3 to 5 ppm) and we can speculate that almost no Cu was translocated to the grains. Our previous data from rice field similarly contaminated with Cu in the same barangay showed that straws with mean Cu of 11 ppm had grains with 4 ppm content (Cuevas et al. 2012).

We can state at this point that there are no health concerns for the people in the Mankayan barangays from consuming rice harvested from their rice fields, even though those are contaminated with Cu, since the Cu content of the grains is well below the limit of 10 ppm (0.5 mg/kg bw) set by the World Health Organization (WHO 1982).

CONCLUSION

This research demonstrated in the field that compost amendment equivalent to 16% and 8% of soil and with rice as test plant can effectively reduce Cu to normal levels of < 30 ppm. These results verified the findings of Fontanilla and Cuevas (2010) in a pot experiment with *Jatropha curcas* as test plant that 20% compost amendment in soil contaminated with available soil Cu of up to 212 ppm was reduced to normal levels. The similar findings of these two studies are: in the study of Fontanilla and Cuevas (2010), soil pH increased from pH 4.6 to 7.6, while in this study, soil pH increased from pH 5.60 to 6.12 with increased compost application; in both studies, soil Cu content is found to be inversely correlated with soil pH and there is greater accumulation of Cu in the plant roots than in the shoots. Therefore, we can conclude that the use of compost is a good remediation strategy for minimizing soil Cu toxicity. Moreover, rice grains harvested from plants grown in compost-remediated Cu-contaminated soil are safe for human consumption. However, based on findings in other countries, we feel we need to investigate the types of organic amendments that can decrease Cu availability, as well as those that can increase the bioavailability of Cu. That will be the subject of future studies.

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CONTRIBUTIONS OF INDIVIDUAL AUTHORS

Virginia C. Cuevas conceptualized the whole research project, got the funding for the research from where this study is part of, formed the hypothesis proven by the study and wrote the manuscript for the article. Joey I. Orajay contributed to the conceptualization of the research project and to the formulation of the hypothesis of the study and data analysis. Cirilo A. Lagman, Jr. did the experiment and collected the data.

CONFLICTS OF INTEREST

None

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