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Impact of Paper Waste and Earthworm on Nutrient and Heavy Metal Content of Rice Straw Compost in the Absence of Manure

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Abstract
Plant residues after harvest are serious problem. In the recycling process of these residues, composting and vermicomposting is an economic, ecologic, and biologic alternative. Recycling of rice straw waste is also difficult due to its degradation resistant structure. Although it is prohibited in many countries, it is still open burned which destroy soil and environment. Paper waste also has a large share in municipal solid waste and is a suitable recycling material. Rice straw wastes are composted and vermicomposted with or without paper waste in the absence of manure. There are significant differences ($p<0.01$) between the treatments for all nutrients and heavy metals. NPK contents are highest in the treatment of Rice Straw Vermicompost (RSV). Mg, Zn and B are also the highest in RSV treatment while Ca, Fe and Cu contents are greater in the treatments Rice Straw Paper Compost (RSPC) and Rice Straw Paper Vermicompost (RSPV). Heavy metal contents are the lowest in Rice Straw Compost (RSC) treatment and increase in the presence of earthworm while all the heavy metal contents are below the limit values. This study also shows it is possible for rice straw to be converted into N rich compost without involving any manure.

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1. Introduction

Rice (*Oryza sativa*) grown widely in Asia, is the World's second cereal with 787.3 million tonnes production quantity and third cereal in harvesting area of 165.3 million hectares in 2021 (FAO, 2023). A significant amount of rice straw remains in the field after rice harvest. The straw/grain ratio is between 0.7 and 1.5, changing with the effects such as crop yield, cutting length, soil characteristics and fertilization (Bakker et al., 2013; Van Hung et al., 2020). Rice straw in the field as a waste, is usually burned to remove the huge waste although burning is not permitted in many countries. Burning the crop residues causes environmental pollution apart from damaging the soil and soil fauna. When rice straw is burn in the field, a combustion process of crop residues emits nitrogen oxides, methane, carbon dioxide, carbon monoxide and sulphur dioxide into the atmosphere (Gadde et al., 2009). Total nitrous oxide emission from crop residue of rice is reported as 173.2 kilo tonnes while burning of crop residues of rice is 6.3 kilo tonnes in 2020 which is still an important environment problem (FAO, 2023).

Rice straw wastes can be valorised in industry (paper and furniture making), in agriculture (animal bedding, mushroom production, incorporation of soil and mulching) and in energy production (Sozubek and Ozturk, 2022). Valorisation of rice straw through composting supports more sustainable environment. Composting is a process that aerobic and microbial degradation usually mixed with other agricultural wastes, manures, green wastes, or inoculants to obtain more homogeneous organic matter. Rice straw generally consists of 30-40% cellulose, 20-30% hemicellulose, 9-15% lignin, 10-20% ash and 5-15% moisture (Sozubek and Ozturk, 2022). Therefore, due to the lignocellulosic structure of rice straw, it is difficult and time-consuming operation to degrade and therefore, it is composted generally with manures, even with the effective microorganisms to accelerate the reactions. Besides, feeding earthworms with rice straw to obtain vermicompost is another way of recovering these wastes. The excreta of earthworm are called vermicompost which have the capability to ameliorate soil health and nutrient status while vermicomposting can be expressed as simple biotechnological process of composting (Adhikary, 2012). Among the most used earthworm species, *Eisenia fetida* is temperature and moisture tolerant (Dominguez and Edwards, 2011). Besides, earthworms can accumulate the high concentration of heavy metals (Singh and Kalamdhad, 2012). Earthworms are sometimes fed with varied materials such as waste paper.

Paper waste is a type of lignocellulosic waste and has the second largest percent in biodegradable materials in municipal solid waste (Zhu et al., 2021). Although depending on income level, paper and paperboard waste is approximately 17% in global waste composition (Kaza et al., 2018). The world generates 0.74 kilogram of waste per capita per day, and world is expected to generate 2.59 billion tonnes of waste by 2030 (Kaza et al., 2018). Global waste treatment and disposal methods include open dump, landfill, sanitary landfill, incineration, recycling, and composting. The composting percentage of waste is 5.5, but some countries report that waste is composted under the recycling category (Kaza et al., 2018). There is research in which paper waste is used as composting substrate that can be valorised as fertilizer (Belliturk, 2016; Gupta and Garg, 2009). Considering that world's paper and paperboard production in 2021 is 417.2 million tonnes, and only printing and writing paper production in 2021 is 82 million tonnes according to FAO (FAO, 2023), recycling processes including composting will gain more importance for environmental protection. Composting wastes to use as fertilizer for a sustainable agriculture is valuable.

Rice straw composts are mainly prepared from additional substrates like chicken manure, donkey manure, goat manure and cow manure as well as effective microorganisms (Jusoh et al., 2013; Wang et al., 2016; Karanja et al., 2019) generally to fasten the composting period by increasing nitrogen content. The application of rice straw composts to the soil as fertilizer, also increase the yields. For instance, rice yield is increased after the substitution up to 50% of inorganic fertilizer with rice straw compost (Watanabe et al., 2009; Sharma and Dhaliwal, 2019;) while dry weight of canola plants is increased by rice straw compost application as well as organic matter of the soil is in-creased three times more than the control (Mahmoud et al., 2018).

Rice cultivation is an important agricultural income in area of the study conducted and rice straw wastes are great problem after harvest. Valorisation of these wastes are needed to avoid field burning, therefore composting and vermicomposting is a rational way of recycling them. For that purpose, the study is designed for recycling both rice straw wastes and paper wastes without adding manure to observe the nutrient content of these organic fertilizers. The aim of this study is to investigate effect of earthworm and paper waste on nutrient and heavy metal content of rice straw compost and to re-veal out the interactions between the heavy metal content in the composting treatments.

2. Materials and Methods

2.1. Substrates and earthworm

Rice straw was taken from the Uzunkopru region near Ergene River in Turkey. Rice straw was chopped to approximately 3 cm size. Waste papers used as document and used in printers are obtained from the offices in the university and waste paper was chopped to approximately 0.2 mm x 2 cm size. Basic elements in the chemical composition of rice straw and paper are given in Table 1. The species of the earthworm used in the study is *Eisenia fetida* and obtained from a commercial breeder. Healthy adult earthworms were selected for vermicomposting.

Table 1. Initial chemical composition of substrates

Element	Unit	Rice Straw	Waste Paper
N	%	1.06	0.22
P	mg kg^{-1}	744	8.55
K	mg kg^{-1}	1218	0.00
Ca	mg kg^{-1}	5709	51995
Mg	mg kg^{-1}	3952	473
Fe	mg kg^{-1}	104.4	987
Mn	mg kg^{-1}	284	11.81
Cu	mg kg^{-1}	1.84	1.77
Zn	mg kg^{-1}	10.53	1.54
B	mg kg^{-1}	11.81	3.70
Na	mg kg^{-1}	1742	0.00
Ni	mg kg^{-1}	4.17	1.77
Co	mg kg^{-1}	0.21	0.20
As	mg kg^{-1}	0.32	0.00
Pb	mg kg^{-1}	0.31	0.00
Al	mg kg^{-1}	66.98	169
Cd	mg kg^{-1}	0.00	0.04
Cr	mg kg^{-1}	0.24	0.71

2.2. Experimental design

This study was conducted in greenhouse conditions using twelve containers with three repetitions. Clean and BPA free polipropylene (PP) containers of two litres are used for compost containers. Small holes are opened in their lids to maintain the optimum humidity conditions. Totally 150 grams of substrates are added to each container. Substrates were adjusted to 70% moisture content by adding deionized water. With the average body weight of 0.4 grams of fifty adult earthworms are added to six of the containers as in the following design as given in Table 2.

Table 2. Description of the treatments in experimental design

Treatment	Rice Straw	Paper	Earthworm #
RSC (Rice Straw Compost)	150 g	-	-
RSV (Rice Straw Vermicompost)	150 g	-	50
RSPC (Rice Straw-Paper Compost)	75 g	75g	-
RSPV (Rice Straw-Paper Vermicompost)	75 g	75 g	50

For composting treatment of only rice straw with 150 grams rice straw (RSC), 150 grams rice straw + 50 earthworms (RSV) for vermicomposting treatment of only rice straw, 75 grams rice straw and 75 grams of paper waste (RSPC) for composting treatment of rice straw and paper waste, 75 grams rice straw and 75 grams of waste paper + 50 earthworms (RSPV) for vermicomposting treatment of rice straw and paper, were designed for the study. The temperature of the room was set constant approximately 22±2 ^{0}C during the study and deionized water was sprayed to maintain 70% moisture. No additional feed was supplied at any stage of composting. The earthworms and cocoons were picked away from the composts after 5 months of experiment period. Composts were prepared for analysis by drying and sieving.

2.3. Chemical analysis

Samples are weighed in aluminium dishes for nitrogen analysis. Total Nitrogen of the samples were analysed at 950 ^{0}C with LECO FP 528 nitrogen/protein determinator according to the AOAC 993.13 method. Then nitrogen reading was performed versus 3-point calibration. Other nutrients and heavy metals were exposed to acid digestion of the mixture of nitric acid and hydrochloric acid in CEM Mars 5 microwave sample preparation machine. After cooled to room temperature, filtered, diluted, and analysed for the elements in Perkin Elmer ICP-OES Optima 7000 DV machine according to TS EN 16963, TS EN 16319+A1 and TS EN 16317 standards (TSE, 2023).

2.4. Statistical analysis

The reported results are the mean of three replicates. Analysis of variance was performed on the data and LSD multiple comparison test was used for comparing the means. The probability levels used for statistical significance were $P < 0.01$. Data analysis was carried out with JMP software.

3. Results and Discussion

Studies on rice straw are mainly designed as composting the wastes with different types of manure. However, self-degradation of rice straw without any manure was the matter of curiosity. The question is partially answered by this study. Due to the resistant cellulosic structure of rice straw, it took a long time to reach the decomposed state. The self-degradation process is controlled with appropriate aeration as well as keeping the temperature and humidity constant. The degradation of cellulosic materials in nature occurs with the cooperation of many microorganisms (Haruta, 2002). There is much research on vermicomposting of rice straw with paper waste by activating with manure. Thereby, organic fertilizers including adequate nutrients become ready to use. In this study, rice straw is both composted and vermicomposted with paper wastes and compared with the controls.

3.1. Macronutrients (N, P, K, Ca, Mg)

Mean values of macronutrient contents and significancy groups are given in Table 3. Significant differences (P<0.01) are found between the treatments for Nitrogen (N), Phosphorus (P) and Potassium (K). The highest N content in the vermicompost was derived from the treatment of RSV (2.52 %), followed by RSC. The lowest N content in RSPC is significantly different from other treatments. Similarly, while the highest P content in the vermicompost from the treatment of RSV (2749.00 mg kg^{-1}), the treatment of paper with only rice straw (RSPC) give the lowest P content. Both vermicomposting and composting of rice straw without paper substrate (RSV and RSC) are the treatments with higher K content (3817.67 and 3501.67 mg kg^{-1} respectively) which are significantly different from other treatments for K.

Table 3. Mean values of macronutrient contents and significance groups

Treatment	**N**	**P**	**K**	**Ca**	**Mg**
	(%)			(mg kg^{-1})	
RSC	2.18 b	1948.67 b	3501.67 a	10788.67 b	7746.33 b
RSV	2.52 a	2749.00 a	3817.67 a	13775.00 b	8828.33 a
RSPC	1.53 c	861.53 d	1599.67 b	24151.67 a	4582.33 c
RSPV	2.13 b	1309.67 c	1530.00 b	26100.00 a	4804.33 c
LSD (P≤0,01)	0.232	232.147	768.961	5085.035	1064.467

Means in columns with different letters indicate significant differences at p<0.01

There are significant differences (P<0.01) between the treatments for Calcium (Ca) in the means of composting with or without paper. On the contrary to N, P and K, the treatments with paper give the highest Ca contents. Ca content of RSPV is the highest (26100.00 mg kg^{-1}) however it is not significantly different from Ca content of RSPC. Like the results of N and P from the same treatments, Magnesium (Mg) content is found the highest (8828.33 mg kg^{-1}) in the treatment RSV. A significant difference (P<0.01) occurs between the treatments in terms of Mg content.

Analysis results show that macronutrient contents (except Ca) are the highest in the treatment RSV and they are significantly different from other treatments at P<0.01. The treatments include paper as substrate, give lower contents of N, P, K and Mg.

According to the statistical analysis of NPK content of the composts, vermicomposting of rice straw without paper substrate gives the highest NPK values. National Ministry of Food, Agriculture and Livestock declares that there should be minimum 0.5 % total N and our results are much more above from this declaration (Anonymous, 2018). Although Ca content of RSPV is the highest, it is not significantly different from Ca content of RSPC which means that earthworm have no significant effect on Ca content in the presence of paper substrate. Significant differences (P<0.01) between the treatments in terms of Mg content shows that treatments including paper have lower Mg contents. The presence of earthworm significantly differs for the benefit of the macronutrient N, P and Mg contents.

3.2. Micronutrients (Fe, Mn, Cu, Zn, B)

On the contrary of the lowest NPK contents in RSPC treatment, the highest Iron (Fe) content (419.73 mg kg^{-1}) is found in this treatment while Fe content was minimum (282.90 mg kg^{-1}) in composting only rice straw treatment (RSC) as seen in Table 4. Addition of paper significantly differs (P<0.01) in Fe content with respect to the treatments that does not contain paper. Manganese (Mn) content of the composts are significantly higher (P<0.01) in RSC treatment than paper and/or earthworm added treatments.

Table 4. Mean values of micronutrient contents and significance groups

Treatment	Fe	Mn	Cu	Zn	B
			(mg kg^{-1})		
RSC	282.90 c	659.33 a	2.24 b	30.00 b	19.28 a
RSV	362.93 b	472.67 b	4.27 b	39.94 a	21.46 a
RSPC	419.73 a	305.67 c	12.79 a	15.80 c	9.66 b
RSPV	396.00 ab	324.00 c	14.03 a	19.64 c	11.10 b
LSD $_{(P\leq0,01)}$	49.762	66.876	4.330	7.065	3.551

Means in columns with different letters indicate significant differences at p<0.01

Similar with Fe content, Copper (Cu) content is higher in the treatment (RSPV) with the value of 14.03 mg kg^{-1} including paper waste and earthworm as well as the treatment RSPC which has the same significance with RSPV. While the highest Zinc (Zn) content is 39.94 mg kg^{-1} in the treatment RSV, it is significantly different from other treatments. However, it is found that the presence of earthworm does not make any significant difference on the microelements of composts of rice straw plus paper waste treatments. Although Boron (B) content in RSV treatment is higher (21.46 mg kg^{-1}) than in RSC, but it is not significantly different (P<0.01). However, B contents in RSC and RSV are significantly higher than that of in RSPC and RSPV which include paper. This shows that B contents in the composts are lower in the presence of paper.

Paper waste addition significantly increases Fe content while Mn content is the highest in the treatment of composting rice straw alone (RSC) which may probably be caused by the initial Mn content of rice straw. Presence of paper also directly differs the results in favour of high Cu content. Although Cu and Zn are essential micronutrients for plants, higher concentrations are possible to be toxic. Nevertheless, maximum concentration of these elements found in this study are far below the limit values which are 450 and 1100 mg kg^{-1} for Cu and Zn respectively given by national regulations (Anonymous, 2018). B contents like Zn, Mn contents are lower in the presence of paper waste. The presence of earthworm does not affect these micronutrients significantly when the treatment was performed with both rice straw and paper.

3.3. Heavy metals and potential toxic elements (As, Ni, Co, Pb, Al, Cd, Cr)

In the study, Arsenic (As) content is the lowest in RSPC, the highest in RSV and there is significant difference (P<0.01) between the treatments as seen in Table 5. Other heavy metals have the lowest contents in RSC. Nickel (Ni) contents of the treatments RSC and RSV are significantly different (P<0.01) between eachother however, RSPC and RSPV treatments are not significantly different (P<0.01) from each other.

Table 5. Mean values of heavy metal and potential toxic element contents and significance groups

Treatment	**As**	**Ni**	**Co**	**Pb**	**Al**	**Cd**	**Cr**
				(mg kg^{-1})			
RSC	2.39 b	1.22 b	0.27 b	0.27 b	133.00 b	0.017 b	0.427 b
RSV	4.04 a	2.23 a	0.92 a	0.38 a	253.33 b	0.103 a	0.783 b
RSPC	1.22 c	1.83 ab	0.40 b	0.27 b	433.00 a	0.043 b	0.983 ab
RSPV	1.94 b	1.75 ab	0.83 a	0.27 b	538.33 a	0.083 a	1.397 a
LSD $_{(P\leq0,01)}$	0.629	0.630	0.223	0.088	135.318	0.032	0.606

Means in columns with different letters indicate significant differences at p<0.01

The presence of paper does not statistically change the Cobalt (Co) content both in the composts and in the vermicompost separately, however the effect of earthworm significantly differs (P<0.01) the results. Lead (Pb) content in the treatments is only different and higher in RSV when compared to the other treatments. Just like Co, Cadmium (Cd) contents are lower in the RSC and RSPC which means that earthworms increase the Cd contents and there are significant differences (P<0.01) between compost and vermicompost.

Aluminium (Al) and Chromium (Cr) contents have similar results. Both Al and Cr have their highest values in RSPV and the lowest values in RSC. There are significant differences (P<0.01) between the treatments including paper or not, but existence of earthworm only does not affect Al and Cr contents. Briefly, As, Ni, Co, Pb and Cd contents are the highest contents in RSV, Al and Cr contents are the highest in RSPV.

Although some heavy metals can also be essential nutrients for some species of plants, there are limits for heavy metals stated in many national and international guidebooks or regulations. When their amounts exceed the limits, then it became unsafe. The treatment RSC gives the lowest content of heavy metals. It seems to be composting of the rice straw without paper waste and earthworm, is the most reliable technique for minimum heavy metal content. The presence of earthworm does not change statistically the Ni content when both rice straw and paper together is allowed to compost. The presence of earthworm significantly effects Co content while paper waste does not significantly affect. Cadmium contents are lower in the RSC and RSPC which means that earthworms increase the Cd contents and there are significant differences (P<0.01) between compost and vermicompost. Lowest Al and Cr values are obtained in RSC.

The results of the analysis show that heavy metal contents are higher in vermicompost when compared to those in compost. Besides, it is reported that metal contents of the composts are often higher than those of initial substrates (Morgan, 2011) so as in this study except for Ni. The increase in the concentration of heavy metals be the result of carbon losses due the mineralisation in the composting process (Dominguez and Edwards, 2011). Nevertheless, all the heavy metal contents are below the permitted limits of heavy metals according to the regulations of Turkey and European Union (Anonymous, 2018; Anonymous, 2019).

3.4. Heavy metal correlations

Heavy metal correlations in all composting treatments are investigated and given in Table 6. Only a few negative correlation (Al with As and Pb, Cr with As and Pb) is detected but these correlations are non-significant either at P< 0.05 or P< 0.01. While others are positive correlations and most of these are non-significant.

Table 6. Correlations between heavy metals in the treatments

	As	**Ni**	**Co**	**Pb**	**Al**	**Cd**	**Cr**
As	1.000	0.407ns	0.531ns	0.779**	-0.466ns	0.514ns	-0.326ns
Ni		1.000	0.655*	0.551ns	0.285ns	0.740**	0.338ns
Co			1.000	0.557ns	0.339ns	0.974**	0.573ns
Pb				1.000	-0.212ns	0.620*	-0.122ns
Al					1.000	0.327ns	0.815**
Cd						1.000	0.523ns
Cr							1.000

*P< 0.05, **P< 0.01, ns: non-significant

In Figure 1, significant positive correlations are shown as chart. Al and Cr have only one significant positive correlation with eachother. Similarly, As have solely one positive correlation with Pb. These are significant at P< 0.01. Pb have another positive correlation with Cd with significancy at P< 0.05 while Cd have the strongest correlation (0.974) with Co. Other significant positive correlation of Cd is with Ni at P<0.01. On the other hand, Co and Ni have smaller positive correlation with eachother.

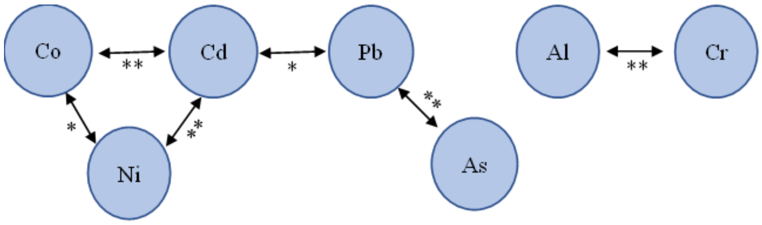

Figure 1. Significant correlation between heavy metals in compost treatments (*P< 0.05, **P< 0.01)

Correlations of some heavy metals are mainly positive but most of them are non-significant. Significant positive correlations of Cd with Co and Ni may be related with similar oxidation states (+2) which can be influential in the composts and further investigation and depth analysis may be needed.

4. Conclusion

Rice straw is composted and vermicomposted with and without paper waste. Since any manure is not used in any step of composting, it took a long time for degradation of rice straw which is resilient cellulosic material. Compost and vermicompost of rice straw have acceptable nutrient contents either with paper waste substrate or not while heavy metal contents are far below the permitted limits in all treatments. Although composts have sufficient nutrients in this study, further investigations to shorten the composting periods without any manure usage in the process are thought to be needed. Composting helps to decrease landfill disposal of paper waste and valorise rice straw waste. It also supports sustainable agriculture by providing value-added products that can be used as domestic or commercial organic fertilizers. Further research including comparison of nutrients of rice straw composts prepared with manure with the ones without manure may be able to support this study. Besides, further application studies of these composts to the plants are planned to investigate the activity of nutrients in the composts prepared.

Declaration of Author Contributions

The authors declare that they have contributed equally to the article. All authors declare that they have seen/read and approved the final version of the article ready for publication.

Declaration of Conflicts of Interest

All authors declare that there is no conflict of interest related to this article.

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