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# **Evaluation of Phosphorus Leaching in an Agricultural Soil under Different Soil Amendments**

ERDONA DEMIRAJ<sup>1\*</sup>, FERDI BRAHUSHI<sup>2</sup>, JAMARBËR MALLTEZI<sup>2</sup>, SULEJMAN SULÇE<sup>2</sup>

<sup>1</sup>PhD Candidate, Department of Agroenvironment and Ecology, Agricultural University of Tirana, 1029 Tirana, Albania <sup>2</sup>Department of Agroenvironment and Ecology, Agricultural University of Tirana, 1029 Tirana, Albania

#### Abstract

The transport of Phosphorus (P) from agricultural soils to surface waters sensitive to eutrophication has long been a world-wide environmental concern. The intensive agricultural activity in the upper Shkodra fields, combined with others point source pollution, probably, intensify eutrophication of the Shkodra Lake. These Clay Loamy soils (calcaric Regosols) are characterized by low organic matter, N and P, with a high water percolation. An experiment was conducted at Greenhouse Research Station, Agriculture University of Tirana, Albania to evaluate Total P (TP) concentration in leaching and runoff waters. A three-month cultivation period of ryegrass (*Lolium multiflorum*) was studied in fourfold replication, while three successive harvests were accomplished under greenhouse conditions. Treatments comprised control soils (without amendment), soil with NPK fertilizer and soils amended with Straw and Biochar. Results of TP leaching tests showed continuous releases of P from fertilizer treatments (NPK without amendments treatment), while on the treatments with organic amendments (Biochar and Wheat Straw) were found to have had a weakened role on TP retention.

Keywords: Total phosphor, biochar, leaching, Clay Loamy soil, NPK fertilizer.

### 1. Introduction

The intensive agricultural activity in the upper Shkodra fields which include the use of mineral fertilizers, combined with the large amount of solid waste and urban wastewater that end up to the lake have negatively influenced and intensified the eutrophication of the Shkodra Lake [3]. Soils in this area affect the quality of water in the lake, while it hosts a diverse biodiversity and numerous sensitive habitats with important economic value [13]. Chemicals used in agriculture activities (fertilizers and pesticides) on the east side of the lake and municipal wastes are considered as the main sources that affecting the water quality in the Albanian side of the Shkodra Lake. The trophic state of this lake is reported as oligotrophic [13].

Several of incoming surface water streams are situated in this part (Rrjolli, Banushi and Vraka creeks and more than 46 wellsprings), which discharge water and other materials - due to erosion and other human activities – to the lake. Land fragmentation with

numerous small private property areas with individual farming activities complicate the control of agrochemicals usage, which in turn increase the value of nutrients (especially phosphate ions) at the East side of the lake, as compared to the Western part [31]. Thus, the control of nonpoint sources of P is a major issue to protecting freshwaters from accelerated eutrophication [42, 40, 47]. The transport of Phosphorus (P) from agricultural soils to surface waters sensitive to eutrophication has long been a world-wide environmental concern. Phosphorus from over-fertilized soil has become an extended environmental issue that contributes to water eutrophication [1]. Sources of P in agricultural runoff include commercial fertilizers and manure. While soluble P concentrations of 0.2 mg/L are required for normal plant growth, currently the increase of fertilizers use in soil contributed to the rapid increase of P, which was measured in soil solution at 8 mg/L, compared to fertilized soil that range from <0.01 to 1 mg /L [38]. Single applications of mineral or organic fertilizers may also cause a direct risk of P loss, especially in cases of fertilizers application of large amounts and/or during conditions with high risk of surface runoff or leaching. This risk is mainly related to soil texture and structure, thus in soils with dominance of macropores is reported a rapid transport of nutrients in soil solutions and particles [23]. Generally, the concentration of P in percolating water through the soil profile is low due to P fixation in subsoil horizons due to their P deficiency. But P leaching through the soil profile is higher in sandy, acid organic or peaty soils with low P fixation or holding capacities and in soils where the preferential flow of water can occur rapidly through macro pores and earthworm holes [41, 5]. Glæsner et al., [18] compared the surface application and injection of dairy slurry and concluded that P leaching from irrigated topsoil columns of clay loam and loam decreased by about half when the slurry was injected. Shoot growth significantly increased by using biochar rate and P fertilizer application under leaching conditions. Plant P uptake increased significantly with organic supplements and biochars because of higher P

content in wheat biochar at about 2%. The increase in plant growth and P uptake can be attributed to the ability of organic amendments and wheat biochar to increase mycorrhizal colonisation, water and P retention in soil and supply to the growing plants [37].

## 2. Materials and Methods

## The study area

The soil samples were collected in the eastern part of Shkodra Lake (Figure 1), which is the largest natural, shallow (mean depth 5m), and fresh water lake of tectonic-karst origin in the Balkan region [37]. Based on FAO Soil Classification [22] and Soil Atlas of Europe [17], soil types found in this area are the Regosols (subtype B - Calcaric Regosol). Regosol soils in the region are about 12,000 ha and situated between the mountainous massif and the Lake's coast. Regosols are formed by deluvions which came from surrounding mountains and are considered as young soils, non-well altered, placed on skeletal and stony materials.



Figure 1. Map of Shkodra Lake (a) and used plot for soil sampling in Gruemira Vilage with yellow color (b).

These soils are characterized by low organic matter, N and P, with a high rate of water percolation. The mineral fraction is dominated by silt and loam fractions, low capacity of cationic exchange (CCE) and adsorption capacity. The special construction of the profile which intensifies the runoff and erosion activities, is further exacerbated due to intensive rains as Shkodra region has an irregular distribution of rainfalls with high intensity [17]. Besides the intensive agricultural activity in the upper Shkodra fields based on the use of artificial fertilizers, the large amount of solid waste and wastewater discharged to the lake negatively affect which and intensify the eutrophication processes in the Lake [11]. Serving as

an agricultural field, this part of the lake is the most ecologically sensible and economically important area [14]. To evaluate the effect of organic substrates such as wheat straw by-product and biochar in the retention of soluble mineral forms of P, an experiment was performed in vegetation pots under controlled conditions. This study was conducted in order to evaluate whether straw and biochar – produced from agricultural residues – could release P in the water, as well as study its potential effect on plant growth and P uptake.

### Soil sampling and analysis

Table 1. The Pots experiment design

Soil samples, were collected in Gruemira village, part of the Koplik municipality in Malesia e Madhe District. A representative soil sample (1kg) from this soil was used to determine physical and chemical parameters. Before set up the experiment, the main soil properties were determined. Thus, the soil texture was determined by Bouyoucos hydrometer method, Total N were determined after digestion with  $H_2SO_4^{cc}$  and  $H_2O_2^{cc}$  of Kjeldahl and Total P were analyzed according to the ascorbic acid molybdenum blue method on Spectrophotometer [12, 36]. The Mehlich III extraction method was used for the determination of available P in soil [32]. N-NO<sub>3</sub><sup>-</sup> determination was conducted based on KCl 2M extraction [6] within 24 hours. The result of Organic Carbon was taken after oxidation of organic matter by

potassium bicarbonate ( $K_2Cr_2O_7$ ) in mixture with  $H_2SO_4^{cc}$  followed by oxidation of ammonium ferrous sulphate (Fe (NH<sub>4</sub>)<sub>2</sub> (SO<sub>4</sub>)<sub>2</sub> x 6H<sub>2</sub>O) based on Walkley, A. and I. A. Black, 1934 [46]. The micronutrients as Mg, Fe, K, Ca were determined with microwave digestion method [33] and then analysed with a Flame Atomic Absorption Spectrometer type AA350. The obtained results on soil properties are presented in the Table 2.

#### Experimental design

The experiment was conducted in four replicates and different treatments at Greenhouse Research Station, Agriculture University of Tirana, Albania. In the Table 1 are presented all six treatments and experimental design.

	Treatments								
Replication	BARE SOIL T1 S	SOIL Lolium T2 SL	SOIL STRAW T3 SS	SOIL NPK Lolium T4 SFL	SOIL STRAW NPK Lolium T5 SSFL	SOIL BIOCHAR NPK Lolium T6			
R1	S1 <sup>1r</sup>	SL2 <sup>1r</sup>	SS3 <sup>1r</sup>	SFL4 <sup>1r</sup>	SSFL5 <sup>1r</sup>	SBFL6 <sup>1r</sup>			
R2	S1 <sup>2r</sup>	$SL2^{2r}$	SS3 <sup>2r</sup>	SFL4 <sup>2r</sup>	SSFL5 <sup>2r</sup>	SBFL6 <sup>2r</sup>			
R3	S1 <sup>3r</sup>	SL2 <sup>3r</sup>	SS3 <sup>3r</sup>	SFL4 <sup>3r</sup>	SSFL5 <sup>3r</sup>	SBFL6 <sup>3r</sup>			
R4	S1 <sup>4r</sup>	SL2 <sup>4r</sup>	SS3 <sup>4r</sup>	SFL4 <sup>4r</sup>	SSFL5 <sup>4r</sup>	SBFL6 <sup>4r</sup>			

The Abbreviation of the above table represent Treatments (**T**) and Replications [n=4] (R); <u>**T1**</u> =0 Bare Soil (7kg) (**S**); <u>**T2**</u> =0 Soil (7kg) + *Lolium multiflorum* (**SL**); <u>**T3**</u> =0 Soil (7kg) + Straw (**SS**); <u>**T4**</u> =0 Soil (7kg) + NPK (**F**) + *Lolium multiflorum* (**L**); <u>**T5**</u> =0 Soil (7kg) + Straw (**SS**) + NPK (**F**) + *Lolium multiflorum* (**L**); <u>**T6**</u> =0 Soil (2kg) + Biochar from Wheat Straw(**B**) + NPK (**F**) + *Lolium multiflorum* (**L**).

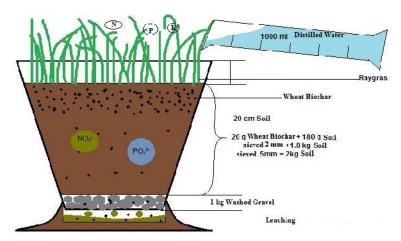


Figure 2. Pot experiment design and leaching sampling.

From the bulk soil samples, stones and plant tissues were removed, and the samples were homogenized, air dried, crushed, and passed through a 5 mm sieve. Plastic pots with dimension  $(22 \times 24 \text{ cm})$  were used in the experiment Figure 2.

The pots, bottom packed with washed gravel 1kg/pot (with a diameter of 1cm), prepared in 6

Treatments with four replicates. Three (3) gram of *Lolium multiflorum* seeds were planted in thoroughly mixed with soil in  $T_2$ ,  $T_4$ ,  $T_5$ , and two gram for  $T_6$  in May 2015.

fertilizer NPK inorganic (15%N:15%  $P_2O_5$ :15% K<sub>2</sub>O) with dose of 300 kg ha<sup>-1</sup> was divided into three doses (3.9 g/pot/dose) in  $T_4$ ,  $T_5$  and 1.11g/pot/dose for  $T_6$  (pots with 2kg of soil). The first fertilization was done at 2/3 leaf stage or in other words 2 weeks after sowing. The second fertilization with the same amount of fertilizer was 1 week after first harvest which was 1 month after planting and the same principle was followed for the third dose of fertilization. The pots were held at 75% Moisture Field Capacity based on the method WFC [2], adding water based on gravimetric method as WFC was calculated in advance. Soil pots were checked daily and water loss was replenished by bringing the pots back to weight.

Organic material such as **Wheat Straw** of <0.1cm minced faction with dose 10 Mgha<sup>-1</sup>, practically 40g/pot for  $T_3$ ,  $T_5$  was used as amendment. Organic fertilizers contain high levels of specific nutrients and they generally have a high organic matter content with a variety of micronutrients [24]. Studies have shown that crop straw is rich in organic material and soil nutrients [31, 45] the addition of crop residues to cultivated soils helps to improve the soil quality and productivity via its favourable effects on soil properties [35]. P concentration in wheat straw is reported about 0.027% or 0.27gkg<sup>-1</sup> [4].

Biochar from wheat as organic material was used with dose 10 Mgha<sup>-1</sup> in T<sub>7</sub>, from which 20g was mixed with 100 g of this soil, previously sieved 2 mm and then was mixed with 1900g soil sieved 5mm. Biochar was the pyrolysis product of wheat straw biomass. As a soil amendment, biochar can greatly influence various soil properties and processes [25]. The presence of biochar in the soil can improve soil chemical (e.g. pH, CEC) [37] and physical properties (e.g. soil water retention, hydraulic conductivity) [30]. Total P concentration on biochar was 1.1 gkg<sup>1</sup> as previously analyzed.

## Plant sampling and analysis

One month after planting, the plants were cut by using laboratory scissors to 2-3 cm from the surface and were encoded taking the wet weight for each crop and the same procedure was performed in the three harvests. Plant samples (*Lolium multiflorum*) collected from the pot experiment were washed uniformly with distilled water to eliminate other materials. Plant samples were placed by spreading on a clean paper sheet, air-dried in an isolated place, dried in an oven at 60<sup>o</sup>C till constant weight, ground in a Wiley mill, and analyzed for Total P based on ammonium molibdate method [29] at Laboratory of the Agro-Environment and Ecology Department, AU of Tirana.

# Soil sampling and analysis

The soil samples were taken with a sterile syringe prepared as probe by plunging in pot 0 - 10 cm, after one month during three harvest process, the syringe was carefully applied to avoid disturbing the soil structure in the pot and the blanks were substituted with clean plastic pipes to maintain precisely this structure. Total P in soil were measured according to the ascorbic acid molybdenum blue method on Spectrophotometer [15]. The syringes with soil samples were labeled by placing the code corresponding to the same treatments and replication.

## Water leaching sampling and analysis

The last water leachate samples were collected from each treatments, by filling the pots with 1000 ml of distilled water in a slow leaching process. From six first treatments respectively  $T_1$ ,  $T_2$ ,  $T_3$ ,  $T_4$ ,  $T_5$  were taken an average 450 ml leach while in  $T_6$  it was drowned with 700 ml of distilled water and was taken an average of 250 ml leaching *Figure 2*. The percolate (leaching) was stored in dark plastic bottles in the refrigerator at a temperature of 4°C and the Total P was analyzed according to the colorimetric methods issued by the International Standard Organization (ISO 15681–12003) within 24 hours [21]. The same procedure was followed for two other harvests during the three months long experiment.

## Statistical analysis

Data collected in three harvests were statistically analysed with the EXEL 2010. The statistically significant differences between groups were tested using the nonparametric Kruskal Wallis test (p < 0.05).

## **3. Results and Discussion**

The result of physical analysis showed that **Clay Loamy Soil (CLS)** with 38.1% of Silt was used for this experiment. The chemical analysis showed higher amount of macro and micro elements in LCS composition.

Soil	Physical characteristics			Chemical characteristics									
type					mg*kg <sup>-1</sup> DW		g*kg <sup>-1</sup> DW						
		(%)			· · · ·								
	pН	Sandy	Silt	Clay	NO <sub>3</sub> <sup>-</sup>	N total	P-total	P available	C organic	Mg	Fe	K	Ca
CLS	8	25,3	38,1	36,6	166.16	1.56	0.673	0.047	19.474	17.292	15.648	4.685	0.797

Table 2. Physical and Chemical characteristics of the soil.

## Leachability of phosphorus

The results of total phosphorus (TP) leached, taken after 3 successive extractions, are provided at the Table 3. Data indicated the differences between fertilizer and non-fertilizer treatments, thus, providing that the TP leached originates mainly from the fertilizers applied.

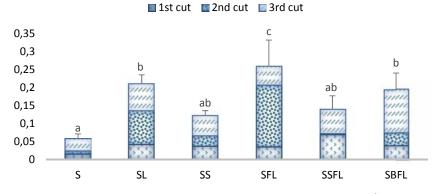
**Table 3.** The mean values and standard deviation for concentration of Total P (TP) on four replications of six treatments in Leaching samples.

Clay	/ Loamy Soil	1 <sup>st</sup> cut	$2^{nd}$ cut $3^{d}$	<sup>rd</sup> cut	Amount TP			
Treatments			LEACHING Average mgL <sup>-1</sup>					
T1	S	$0.016 \pm 0.011 \ ^{a*}$	$0.009 \pm 0.004 \ ^a$	$0.034 \pm 0.009 \; ^{\rm a}$	$0.059\pm \ 0.0078\ ^{a}$			
T2	SL	$0.043 \pm 0.016 \ ^{b}$	$0.093 \pm 0.071 \ ^{b}$	$0.075 \pm 0.004 \ ^{b}$	$0.211 \pm 0.0301 \ ^{b}$			
Т3	SS	$0.038 \pm 0.019 \ ^{b}$	$0.029 \pm 0.010^{\ c}$	$0.056\pm0.010~^{ab}$	$0.123 \pm 0.0131 \ ^{ab}$			
T4	SFL	$0.036\pm0.011^{b}$	$0.171 \pm 0.113^{\ d}$	$0.052\pm0.015~^{ab}$	$0.259 \pm 0.0463$ <sup>c</sup>			
T5	SSFL	$\textbf{0.07} \pm \textbf{0.048}^{\text{ c}}$	$0.003 \pm 0.002 \ ^a$	$0.067 \pm 0.010 \ ^{ab}$	$0.14 \pm 0.0199 \ ^{ab}$			
T6	SBFL	$0.039 \pm 0.006^{\;b}$	$0.036 \pm 0.005 \ ^{c}$	$0.119 \pm 0.024$ <sup>c</sup>	$0.194 \pm 0.0115 \ ^{b}$			

\*Means ± standard deviation, Small letters (a, b and c) indicate significant differences within each table column (=0.05; n=4)

It was found that the average TP value leached in  $T_4$  was higher compared with all other treatments (Figure 3). The results obtained in  $T_5$  and  $T_6$  are significantly lower compared with  $T_4$  due to the addition of the Straw and Biochar amendments. The differences between the  $T_5$  and  $T_6$  were observed in the second and third harvests. In the second harvest the TP amount in leaching was higher in those treatments where straw was added, likely a result of the rapid

effect of Biochar compared to Straw amendments. In the third harvest a weakened role of the Biochar in TP retention accompanied with an enhanced role of Straw were observed in the process. The results of both treatments  $T_5$  and  $T_6$  indicated that the Biochar had a short-time effect in TP retention compared to Straw but in total the use of organic amendments decreased TP leached from the soil.



**Figure 3.** TP accumulated in three successive Leaching process on 3-Cuts (1, 2 and  $3^{rd}$  cut) in mgL<sup>-1</sup>. Small letters (a, b and c) indicate significant differences within each graph column (=0.05; n=4).

According to Water Quality Standard the TP should be lower than  $5-10\mu g L^{-1}$  in lake water but in the agriculture water discharges (leaching) in three cuts the values were beyond the limit. The order from the highest to the lowest concentration of P released in relation to the total P was: SFL>SL>SBFL>SSFL>SS>S.

Phosphorus leaching is reported to be strongly correlated to soil texture [26]. Thus, in Clay Loamy soil was found up to 1.50 mg L<sup>-1</sup> Total P concentration after applying mineral P fertilizer, as reported by Liu

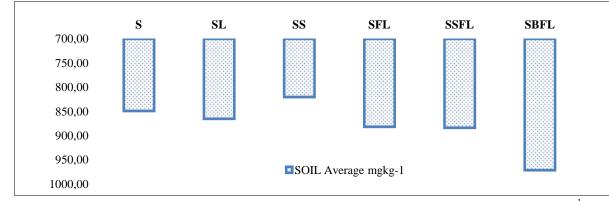
Impact of Straw and Biochar on total P in soil

et al., [28]. The amendement of biochar to alkaline soils is likely to increase absorption and decrease availability of P [9] since the presence of alkaline metals would only exacerbate Ca-driven P limitations. Biochar contains a large amount of P and may therefore directly release soluble P and enhance its availability, especially for short-term uses [8]. Biochar may also alter P availability through sorption of chelating organic molecules like phenolic acids, amino acids and complex proteins or carbohydrates [10].

Table 4. The mean values found in treatments for Total Phosphor in soil samples.

Treatments		1 <sup>st</sup> cut	2 <sup>nd</sup> cut	3 <sup>rd</sup> cut	Average TP of three Cuts	
			SOIL Average mgkg <sup>-1</sup>			
T1	S			$849.33\pm9.81$	$849.33\pm9.81$	
T2	SL	$711.44 \pm 146.94$	$957.43 \pm 151.21$	$927.88\pm60.83$	$865.58 \pm 119.66$	
T3	SS	$532.71 {\pm} 40.74$	$962.13 \pm 69.77$	$967.06\pm61.52$	$820.63\pm57.34$	
T4	SFL	$593.70\pm17.58$	$1031.38\pm84.12$	$1021.34\pm5.60$	$882.14\pm35.77$	
T5	SSFL	$592.01 \pm 21.36$	$1007.29 \pm 62.67$	$1052.50 \pm 55.20$	$883.93 \pm 46.41$	
T6	SBFL	$878.10\pm31.11$	$1037.76 \pm 56.06$	$998.46\pm74.65$	$971.44 \pm 53.94$	

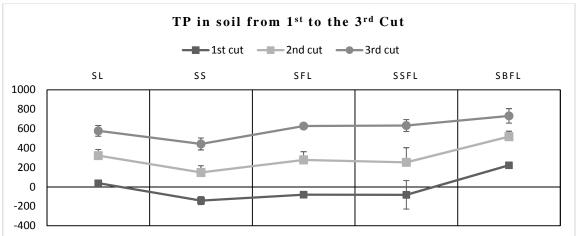
The result of Table 4 did not show a difference between  $T_4$  and  $T_5$  during three cuts, but a different behaviour of biochar was noted from the first to the third cut. In general, lower value of TP were observed in the first cut for  $T_3$ ,  $T_4$ ,  $T_5$ , as compared to  $T_6$  and  $T_2$ . There was a difference between the first and the second cut, likely as a consequence of the addition of NPK as fertilizer  $(T_3-T_5)$ . Concentrations of P in biochars were several times higher than in unpyrolyzed organic materials rendering biochar a potential P soil amendment [7]. Many studies reported on biochar itself being a potential P source [43, 20, 44, 9, 48].



**Figure 4.** Average Total P values found in plant tissues of each treatments, expressed as average mg kg<sup>-1</sup>Soil

The results given in Figure 4 express the average value of the TP measured by the analysis made in each harvest, from which it becomes clear that the biochar (SBFL treatment) has played an important role in the TP retention. Contrariwise, the wheat straw (SSFL treatment) has not affect the

impacting TP value, by having almost equal value to treatment where only NPK were used (SFL treatment). The difference was obvious in SS treatment were the TP values, in terms of average, were lower compared to the control, explaining the active role of microorganisms over decomposition process of organic matter and TP consumption for their metabolism needs.



**Figure 5.** Average TP concentration in soil as difference value between treatments and control one. From five treatments the TP value of control was removed.

To evaluate the added TP value from the firs harvest in the third one, a comparison was made between different treatments value as average and the TP value (serving as control) found on soil at the beginning of the experiment (Figure 5). During the first cut in all the treatments the TP were added or fixed to the soil expected here the SBFL treatment. This trend were observed during the three harvests with the highest amount of TP accumulated in biochar treatment.

### Straw and Biochar effect on P uptake

Phosphorus uptake by *Lolium multiflorum* is the product of the plant yield and the P concentration in

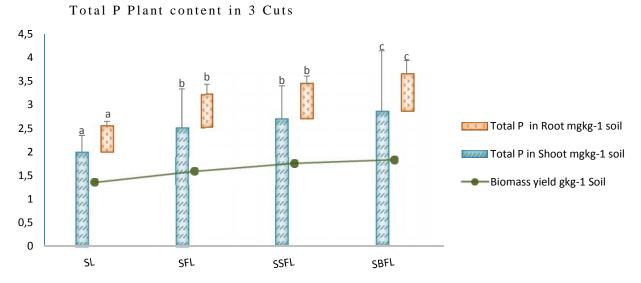
*Lolium multiflorum*, which are depicted at Table 5 provided below. Plant yields (Shoot + Root) derived from the 3 harvests are shown in Table 5 as well. In first and second harvest, biochar applications demonstrated positive significant difference (P < 0.05), compared to the control. However, in the third harvests both SFL and SSFL treatments showed positive significant difference (P < 0.05), compared to the SL control.

Treatments		Yield 1 <sup>st</sup> Cut	Yield 2 <sup>nd</sup> Cut gkg <sup>-1</sup> Soil	Yield 3 <sup>rd</sup> Cut	Biomass yield (gkg <sup>-1</sup> Soil)*	Total P shoot Uptake 3 Cuts <sup>†</sup>	Total P root Uptake TP mgkg <sup>-1</sup> Soil	Total P plant Uptake <sup>‡</sup>
T2	SL	0.464	0.264	0.337	1.358	2.00	0.556	2.56
T4	SFL	0.437	0.357	0.500	1.588	2.51	0.698	3.21
T5	SSFL	0.488	0.370	0.534	1.755	2.69	0.747	3.43
T6	SBFL	0.540	0.563	0.351	1.830	2.85	0.791	3.64

Table 5. Amount of TP plant content and plant uptake in different treatments.

\*Biomass yield is amount of Shoot part in 3 Cuts; †Amount of Replications [n=4] Mean value in 3 Cuts ( $1^{st}$  Cut +  $2^{nd}$  Cut +  $3^{rd}$  Cut); ‡ Amount of TP content in Shoot part and Roots part of the plant.

The results of Total Phosphorus absorption by plant showed that were higher in  $T_5$  and  $T_6$ . The TP uptake, from the *Lolium multiflorum* were influenced by the organic matter. No fundamental changes were observed between the treatment with wheat straw SSFL and the treatment with biochar SBFL in shoot part of the plant and remained the same in the root too Figure 6.



**Figure 6.** The trend biomass yield and TP shoot uptake compare to the root uptake. Small letters (a and b) indicate significant differences within each graph column (=0.05; n=4).

## 4. Conclusions

Intensive agriculture generates large quantities of nutrient-rich agricultural wastes that could be applied to soils enhancing crop production and reducing the amount of needed chemical fertilizers. The results from this study suggest that biochars derived from wheat straw as pyrolyzed agricultural residues, had the potential to release phosphorus into the water phase continuously and gradually compared with raw biomass like wheat straw. The addition of NPK together with different amendments showed positive effects on plant yield, although statistically positive significant differences were observed in treatments with straw and biochar amendments. Arguable effects with plant yield were observed for P leached from soil, where positive significant differences were detected in different harvests. The highest amount of TP leached in three successive leaching processes was found in SFL (T<sub>4</sub>) treatment. Despite the fact that leaching tests and pot experiments were a good starting point for assessing biochar-soil-plant systems under natural conditions, the most reliable data could be obtained by experiments under field conditions with different type of soils and plants.

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