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The Application of a Bio-Stabilized Municipal Solid Waste-Based Fertilizer for Buckwheat Production

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Abstract: In a circular economy framework, waste valorization in crop production promotes sustainability in the agricultural sector. Buckwheat (BW; *Fagopyrum esculentum* Moench) has promising nutritional and economic value. Its sustainable production can be promoted by applying organic fertilizers. Aimed at determining the effect of a bio-stabilized municipal solid waste (MSW) amendment on BW, a greenhouse experiment was performed combining two different soils (clay and sandy) with three previous fertilization treatments (no fertilizer, mineral fertilizer, or MSW fertilizer) from the precedent faba bean crop and three present fertilization treatments (no fertilizer, mineral fertilizer, or MSW fertilizer) from the precedent wheat crop. The present fertilizer treatments followed the same procedure and fertilization rates (7.9 g/kg clay soil and 6.7 g/kg sandy soil of MSW amendment and 0.14 g/kg clay soil and 0.12 g/sandy soil of mineral fertilizer) as the previously fertilized treatments to study the effects on BW crop and soil. Results indicated a positive response of biomass production (on average 34.4 g/plant) and seed yield (on average 10.6 g/plant) to direct organic fertilization, obtaining comparable results with respect to the mineral fertilization treatments. Additionally, organic fertilization significantly enhanced seed quality and nutrient content compared to mineral fertilization, which resulted in a higher chlorophyll content. The findings revealed that the residual effect from the previous bio-stabilized MSW amendment was not sufficient to provide the total nutrients necessary for BW potential growth and biomass production, although slight tendencies toward increase were observed. Soil properties, such as organic matter and nitrogen content, as well as soil nutrient concentrations, were positively affected by organic fertilization, presenting adequate levels of heavy metals (Cu, Zn, Pb, Ni, Cr, and Cd). The insights of this study are valuable to determine the effects of reusing waste by-products for BW crop fertilization to reduce or substitute for chemical fertilizers.

Keywords: fertilization; pseudocereal; by-product waste; soil; organic fertilizer

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1. Introduction

Buckwheat (BW; *Fagopyrum esculentum* Moench) is a pseudocereal that has recently become a popular crop because of its positive effects on human health. It can serve as a source of antioxidants, vitamins, proteins, resistant starch, minerals, and dietary fibers [1], and its consumption is suitable for gluten-sensitive and hypertensive people [2]. It is also used as forage plants for animal feed, weed control, erosion prevention, and green manure, among other uses [3]. This pseudo-cereal belongs to the Polygonaceae family and comes from Central Asia. Driven by the increasing consumption of BW, its production has also increased in the past years [4], with China and Russia being the main producers, followed by Ukraine, France, and Poland. BW is an annual crop that can be grown as a stand-alone crop or in rotation with other crops [5]. It presents high tolerance to soil acidity and is capable of growing in nutrient-poor soils better than other seeds [6]. Although BW can grow to some extent in poor soils, BW yield and seed yield can be enhanced by fertilization [7].

Intensive agricultural production is one of the main contributors to global greenhouse gas emissions, particularly caused by the excessive application of nitrogenous fertilizers [8]. To reduce greenhouse gas emissions and promote more sustainable agricultural practices, organic amendments can be used solely or combined with mineral fertilizers [9]. Organic fertilizers can positively affect the physicochemical and biological aspects of the soil and can favor the soil's nutrient content [10]. Several organic amendments have been used in crop production [11–13]. In particular, benefits have been observed from the application of different organic amendments in cereal production [14–16].

Bio-stabilized municipal solid waste (MSW) amendment can be used as a source of organic fertilization. The organic fraction of MSW is reused and recycled for agricultural purposes as nutrient and organic matter sources [17]. The MSW undergoes bio-stabilization processes, such as composting, to finally obtain organic fertilizers. According to a Spanish regulations, the organic fertilizer compost is achieved through a selective collection of material, while bio-stabilized MSW amendments are obtained from non-source separated municipal solid wastes [18]. Previous studies have shown the positive effects of organic amendments on BW. The use of vermicompost led to a significant increase in the N and P content in BW seeds [19]. Similarly, natural fertilization with manure obtained a positive response of N and nutrient content on BW and the chemical properties of the soil [7]. Additionally, the complex mixture of organic mineral fertilizers exhibited a positive influence on some BW varieties, increasing crop productivity [20].

Crop rotation is widely recognized as a soil and crop productivity improvement strategy. Rotation systems promote the efficient use of resources, enhance soil fertility and structure, increase crop yield, and reduce soil erosion, among other benefits [21]. Rotating crops with gramineous plants could be used to correct iron nutrition deficiencies by enhancing iron and chlorophyll concentrations in plants [22]. Additionally, legume-based crop rotation systems improve soil fertility and increase phosphorus and nitrogen availability [23]. It has been reported that crop rotation systems with cereals and legumes promote the uptake of nitrogen, resulting in higher crop yields [24–26]. Furthermore, the continuous nitrogen input through fertilization on crop production systems could have a residual effect that increases the soil nitrogen availability [27]. The residual effect of organic fertilization can be seen by the increase in soil organic carbon content and crop production [28], and the combination of mineral fertilizers with organic wastes, such as MSW, can even enhance this residual effect [29]. The type of soil can also influence crop yield. Crop yield increases with optimal nitrogen application, and it has been found that in cereal crops such as rice, the yield could be higher in clay soils than in sandy soils [30]. Similarly, leguminous crops, such as faba bean, yield better in well-structured soils with high clay content [31]. The presence of clay in soils can prevent nutrient leaching [32], and the increase in crop production could enhance the crop residual effect, favoring soil nitrogen accumulation by the fixating capacity of faba bean nodules [33].

As BW demand increases, so does BW production. Therefore, fertilizers that provide high crop production as well as guarantee the protection of the environment, are required. Agriculture production has been strongly reliant on non-renewable mineral fertilizers, and the application of organic fertilization in agricultural systems can be an alternative source of exogenous nutrients for crops and soils. This work aims to contribute to the existing literature by studying the effects of the direct application of a bio-stabilized MSW amendment on BW production and seed quality. Additionally, BW's ability to develop under different fertilizer/previous crop residual effects will be studied as a tool to increase the nutrient use efficiency of the cropping system. Finally, all these effects will be evaluated under clay and sandy soil conditions. It is believed that BW treatments with the residual effect of faba bean crop will exhibit higher BW yield and nutrient content than the treatments with the residual effect of wheat, because of faba bean's ability to fix N_2 and to benefit following crops. In addition, significant differences are expected between the control and the previously fertilized treatments. Improved soil and crop properties are expected for the treatment with MSW residual effect as the MSW amendment provides high nutrient content. In the same way, direct application of MSW is expected to result in higher crop yield and enhanced crop and soil properties with respect to mineral fertilization and the control treatments.

2. Materials and Methods

2.1. Experimental Design

An experiment with buckwheat (BW) was conducted in a greenhouse at the National Institute for Agricultural Research (INIA), located in Madrid (Spain), sown on 15 February 2021. The experiment consisted of a total of 36 pots of twelve liters of capacity distributed in a randomized complete block design. It combined 2 different soils (clay and sandy) with 6 different nutrient availability situations: 3 nutrient availability situations consisted of the soil from a precedent faba bean crop with residual fertilization effect (0 fertilizer, mineral fertilizer, or MSW fertilizer), and the other 3 nutrient availability situations consisted of the soil from a precedent wheat crop with present fertilization (0 fertilizer, mineral fertilizer or MSW fertilizer). A total of 12 treatments (6 fertilization treatments and two types of soils) with 3 replications were carried out. The duration of the precedent fertilization studies with precedent faba bean and wheat experiments was approximately the same. The 6 different nutrient availability situations were as follows:

- NFW_NF: unfertilized wheat (NFW) as precedent crop and without BW fertilization (NF).
- NFF_NF: unfertilized faba bean (NFF) as precedent crop and without BW fertilization (NF).
- MinF_RMin: residual mineral fertilized faba bean (MinF) as precedent crop and without BW fertilization, only residual fertilizer effect (RMin).
- MSWF_RMSW: MSW fertilized faba bean (MSWF) as precedent crop and without BW fertilization, only residual fertilizer effect (RMSW).
- MinW_Min: mineral fertilized wheat (MinW) as precedent crop and with present mineral BW fertilization (Min).
- MSWW_MSW: MSW fertilized wheat as precedent crop (MSWW) and with present MSW BW fertilization (MSW).

The two types of soils used were sandy soil (92% sand, 5% clay, and 3% silt) and clay soil (35% clay, 37% silt, and 28% sand). The properties of the bio-stabilized amendment from MSW are defined in Table 1. The bio-stabilized amendment from MSW was provided by the Urbaser Company [34] and was applied at a rate of 115 g/pot (7.9 g/kg clay soil and 6.7 g/kg sandy soil) [35]. The mineral fertilizer used was a 15-15-15 complex (N-P_2O_5-K_2O) and was applied at a rate of 2 g/pot (0.14 g/kg clay soil and 0.12 g/sandy soil). The fertilization rates with the mineral fertilizer and MSW amendment were the same for the precedent faba bean crop and for the present BW crop. As the composition of both fertilizers was different, the fertilizer rates were adjusted in order to obtain a similar balance for N and P. The final rates applied were around 41 kg P_2O_5 ha^{-1} for the MSW and 50 kg P_2O_5 ha^{-1} for the mineral and around 66 kg N ha^{-1} for the MSW and 50 kg N ha^{-1} for the mineral. The initial soil properties for each one of the 12 initial nutrient availability situations are defined in Table 2. Nineteen seeds of BW were sown in each pot. Throughout the experiment, plants were watered, maintaining a humidity of approximately 60% of the soil's water-holding capacity, and kept weed-free.

Table 1. Physicochemical properties of the bio-stabilized municipal solid waste amendment (MSW) in dry matter.

Parameter	MSW	Parameter	MSW	Parameter	MSW
Humidity (%)	78.8	Ratio C/N	13.48	Co (mg/kg)	<1.00
Ashes (g/kg)	39	$N\text{-}NH_4^+$ (mg/kg)	3174.5	Mn (mg/kg)	92.4
pH,1:2.5 H_2O	6.8	$N\text{-}NO_3^-$ (mg/kg)	208.32	Zn (mg/kg)	140
E.C.,1:5 H_2O (dS/m)	5.59	P_2O_5 total (g/kg)	2.1	As (mg/kg)	1.7
Humic acids (%)	8.3	K_2O total (g/kg)	10.9	S (mg/kg)	6822.8
Fulvic acids (%)	8	CaO total (g/kg)	68.6	Cu (mg/kg)	92.4
Humic extract (%)	16	MgO total (g/kg)	69.7	Cr (mg/kg)	31.9
Organic carbon (%)	17.46	Na total (g/kg)	7.8	Ni (mg/kg)	5.4
Organic matter (%)	30.01	Al (mg/kg)	2600	Mo (mg/kg)	<1.00
N Kjeldahl (%)	1.29	Fe (mg/kg)	5010	Pb, Cd (mg/kg)	26

Table 2. Soil chemical properties of the different nutrient availability treatments at the beginning of the experiment. Different letters represent significant differences among treatments ($p < 0.05$).

Soil Properties	Soils	Treatments					
		NFW_NF	NFF_NF	MinF_RMin	MSWF_RMSW	MinW_Min	MSWW_MSW
pH	Sandy	7.35 d	7.71 c	7.91 b	8.03 a	7.46 d	7.91 b
	Clay	7.65 d	7.82 c	7.91 b	8.06 a	7.84 bc	8.00 ab
E.C. (dS/m)	Sandy	0.06 b	0.07 b	0.11 a	0.11 a	0.07 b	0.10 a
	Clay	0.10 ab	0.09 b	0.11 a	0.11 a	0.12 a	0.12 a
Organic Matter (%)	Sandy	0.50 d	0.67 b	0.69 ab	0.72 a	0.53 d	0.60 c
	Clay	0.50 d	0.67 b	0.69 ab	0.73 a	0.58 c	0.68 ab
N Kjeldahl (%)	Sandy	0.06 b	0.08 ab	0.09 a	0.10 a	0.07 ab	0.08 ab
	Clay	0.07 a	0.07 a	0.09 a	0.10 a	0.08 a	0.09 a
P_2O_5 (g/kg)	Sandy	0.30 c	0.60 b	0.80 a	0.90 a	0.50 b	0.70 ab
	Clay	0.40 b	0.50 b	0.70 a	0.70 a	0.60 ab	0.70 a
K_2O (g/kg)	Sandy	4.80 bc	5.10 b	4.30 c	6.10 a	5.20 b	5.70 ab
	Clay	4.30 b	4.50 b	4.70 ab	5.30 a	4.80 ab	5.10 a
CaO (g/kg)	Sandy	30.00 c	31.00 c	36.00 ab	36.90 a	34.80 b	35.20 b
	Clay	34.30 c	35.80 bc	36.10 b	37.30 a	35.00 c	35.80 bc
MgO (g/kg)	Sandy	3.00 c	3.50 bc	4.10 a	4.40 a	3.70 b	4.00 ab
	Clay	3.00 b	3.50 ab	4.20 a	4.10 a	3.80 ab	4.00 a
Zn (mg/kg)	Sandy	15.00 c	15.77 c	28.33 b	35.57 a	25.4 b	30.33 ab
	Clay	17.20 c	19.36 c	27.1 b	36.53 a	26.31 b	36.53 a
Cu (mg/kg)	Sandy	17.92 c	18.63 bc	23.10 b	32.40 a	20.32 b	30.50 a
	Clay	17.81 c	16.90 c	22.73 b	30.13 a	21.17 b	28.50 a
Cr (mg/kg)	Sandy	5.41 c	5.41 c	16.58 b	21.43 a	16.02 b	20.3 a
	Clay	7.22 c	7.26 c	12.97 bc	24.93 a	16.12 b	23.4 a
Ni (mg/kg)	Sandy	4.77 b	4.85 b	5.96 b	16.30 a	5.31 b	15.83 a
	Clay	4.68 b	4.68 b	5.76 b	16.49 a	5.27 b	15.50 a
Pb, Cd (mg/kg)	Sandy	<0.20 a	<0.20 a	<0.20 a	<0.20 a	<0.20 a	<0.20 a
	Clay	<0.20 a	<0.20 a	<0.20 a	<0.20 a	<0.20 a	<0.20 a

NFW_NF: unfertilized wheat as precedent crop and without BW fertilization; NFF_NF: unfertilized faba bean as precedent crop and without BW fertilization; MinF_RMin: residual mineral fertilized faba bean as precedent crop and without BW fertilization, only residual fertilizer effect; MSWF_RMSW: MSW fertilized faba bean as precedent crop and without BW fertilization, only residual fertilizer effect; MinW_Min: mineral fertilized wheat as precedent crop and with present mineral BW fertilization; MSWW_MSW: MSW fertilized wheat as precedent crop and with present MSW BW fertilization.

2.2. Soil and Crop Physical and Chemical Analyses

Along the entire crop cycle, crop height and leaf pigment content were measured periodically. Crop growth (as total plant height) was monitored from March to May 2021 when seeds were collected. Leaf pigment (chlorophyll, flavonols, and anthocyanins) content was measured along the crop cycle at the last completely extended leaf with the non-destructive Dualex® Scientific (Force-A, Orsay, France) leaf clip sensor. BW seeds, biomass, and soil samples were harvested at the end of May for crop and soil analyses. BW seeds and biomass were separated and dried in an oven and weighted to determine crop yield. Prior to analyzing nitrogen content, BW seeds and biomass were ground into a fine powder with a laboratory mill. The Kjeldahl method was used to determine the total Kjeldahl nitrogen and was then converted to protein by multiplying the total nitrogen concentration by 6.25 [36]. Once the BW seeds were milled, the nutrient content of calcium (Ca), chromium (Cr), copper (Cu), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), nickel (ni), phosphorus (P), zinc (Zn), and lead (Pb) was analyzed by acid digestion and determined using inductively coupled argon plasma optical emission spectrometry (ICP-OES) [37].

Regarding soil analyses, soil samples from each plot were sieved through a 2 mm sieve, homogenized, and kept in the laboratory at 4 °C before carrying out the analyses. Soil pH was measured with a glass electrode (pHmeter BASIC20, Crison, Barcelona, Spain) using a soil water suspension of 1:2.5 (w/v), and the electrical conductivity (E.C.) was determined with a conductometer (soil/water ratio, 1:5.0: conductometer CDM3 Radiometer, Copenhagen, Denmark) at 25 °C [38]. The Kjeldahl method was used to determine the total Kjeldahl nitrogen, and the Walkley and Black method [39] was applied to obtain the organic carbon. Inductively coupled argon plasma emission spectrometry (ICP-OES, Perkin Elmer, Waltham, MA, USA) [37] was used to determine the elements P, K, Ca, Mg, and heavy metals Cu, Zn, Pb, Ni, Cr, and cadmium (Cd) by applying acid digestion using concentrated HNO_3 and $HClO_4$ [40].

2.3. Statistical Analysis

The collected data were analyzed using IBM SPSS software (version 25) [41]. A two-way analysis of variance (ANOVA) was performed to compare the effects of fertilization and the type of soil on the measured variables. Significant differences were determined using the Tukey HSD test at $p < 0.05$.

3. Results

3.1. Previous Crop Residual Effect on BW Crop

The effect of the residue from the previous crop was analyzed between treatments NFW_NF and NFF_NF. The only difference between these two treatments was the previous crop, as no fertilization was used during the previous or the present year. The precedent crop did not present significant differences in BW yield (Table 3). A small increase in yield after the faba bean was observed in the sandy soil, but it was not significant. On the other hand, with respect to the clay soil, the wheat residual effect significantly influenced BW height (Figure 1). Regarding the pigment content, the effect of the residue from the previous crop did not lead to large differences. Chlorophyll was influenced by the previous crop during the middle of the experiment in the sandy soil, exhibiting significant differences, while in the clay soil, the differences were observed at the beginning of the experiment. For the flavonols, significant differences during the middle of the experiment were observed for both types of soil. In general, anthocyanins were not influenced by the previous crop residue. Nutrient content in biomass presented significant differences in calcium, copper, potassium, magnesium, manganese, and zinc in the sandy soil and potassium, manganese, phosphorus, and zinc in the clay soil.

Table 3. Effect of organic fertilization with bio-stabilized MSW amendment and mineral fertilization on buckwheat yield, seed yield, quality, and nutrient content (n.d.: no detection). Factors' effect over the measured variables was assessed as not significant (ns) or statistically significant (*) for $p < 0.05$ (mean values with different letters in the same row vary significantly).

Parameter	**Soils**	**Treatments**						**Soil**	**Treatment**	**Soil × Treatment**
		NFW_NF	**NFF_NF**	**MinF_RMin**	**MSWF_RMSW**	**MinW_Min**	**MSWW_MSW**	***p***	***p***	***p***
Biomass yield (g/plant)	Sandy	12.72 c	12.82 c	14.91 b	18.42 b	34.03 a	35.61 a	ns	*	ns
	Clay	18.82 c	20.10 c	21.65 bc	27.76 b	35.50 a	39.20 a			
Seed yield (g/plant)	Sandy	3.79 c	4.45 c	5.26 b	5.52 b	7.98 ab	9.87 a	*	*	ns
	Clay	5.44 c	5.52 c	6.21 b	6.35 b	10.83a	11.23 a			
Nitrogen (%)	Sandy	0.89 d	0.95 d	0.97 cd	1.01 c	1.49 b	1.87 a	ns	*	ns
	Clay	1.04 d	1.11 cd	1.13 cd	1.18 c	1.51 b	1.88 a			
Protein (%)	Sandy	5.58 d	5.91 cd	6.04 c	6.32 c	9.28 b	11.66 a	ns	*	ns
	Clay	6.48 d	6.91 cd	7.07 c	7.36 c	9.43 b	11.74 a			
CaO (g/kg)	Sandy	0.03 c	0.05 b	0.05 b	0.05 b	0.04 bc	0.06 a	*	*	*
	Clay	0.05 b	0.04 b	0.05 b	0.05 b	0.07 a	0.06 ab			
Cr (mg/kg)	Sandy	1.24±	1.23	1.25	1.76	1.27	1.78	-	-	-
	Clay	n.d.	0.59	0.88	1.01	n.d.	1.03			
Cu (mg/kg)	Sandy	7.12 b	6.28 c	6.77 c	7.20 ab	6.75 c	7.56 a	*	*	*
	Clay	4.59 bc	4.54 c	4.98 b	5.47 a	4.99 b	5.12 a			
Fe (mg/kg)	Sandy	54.94 b	53.28 b	54.89 b	78.23 a	55.57 b	80.71 a	*	*	*
	Clay	37.12 b	32.86 b	37.12 b	39.17 ab	39.46 ab	41.63 a			
K_2O (g/kg)	Sandy	6.20 b	5.70 c	5.90 bc	6.00 bc	6.30 b	6.50 a	ns	*	ns
	Clay	5.00 b	4.30 c	4.60 bc	4.90 bc	5.30 a	5.40 a			
MgO (g/kg)	Sandy	3.60 a	3.00 b	3.10 b	3.10 b	3.40 ab	3.40 ab	ns	*	ns
	Clay	3.00 b	2.90 b	3.00 b	3.10 b	3.30 ab	3.70 a			
Mn (mg/kg)	Sandy	5.77 d	4.15 e	7.39 c	8.07 b	7.88 bc	8.98 a	*	*	*
	Clay	6.89 d	5.69 e	7.47 cd	9.00 b	7.89 c	10.85 a			
Ni (mg/kg)	Sandy	n.d.	n.d.	0.53	1.04	n.d.	1.38	-	-	-
	Clay	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.			
P_2O_5 (g/kg)	Sandy	7.20 b	7.30 b	7.40 b	7.50 b	7.60 b	9.30 a	*	*	*
	Clay	6.9 b	4.80 c	6.00 b	7.40 ab	8.00 ab	8.60 a			
Zn (mg/kg)	Sandy	26.39 c	41.99 b	47.31 ab	52.51 a	36.52 bc	56.39 a	*	*	*
	Clay	25.00 b	29.62 a	29.90 a	30.34 a	28.75 a	29.98 a			
Pb (mg/kg)	Sandy	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	-
	Clay	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.			

NFW_NF: unfertilized wheat as precedent crop and without BW fertilization; NFF_NF: unfertilized faba bean as precedent crop and without BW fertilization; MinF_RMin: residual mineral fertilized faba bean as precedent crop and without BW fertilization, only residual fertilizer effect; MSWF_RMSW: MSW fertilized faba bean as precedent crop and without BW fertilization, only residual fertilizer effect; MinW_Min: mineral fertilized wheat as precedent crop and with present mineral BW fertilization; MSWW_MSW: MSW fertilized wheat as precedent crop and with present MSW BW fertilization.

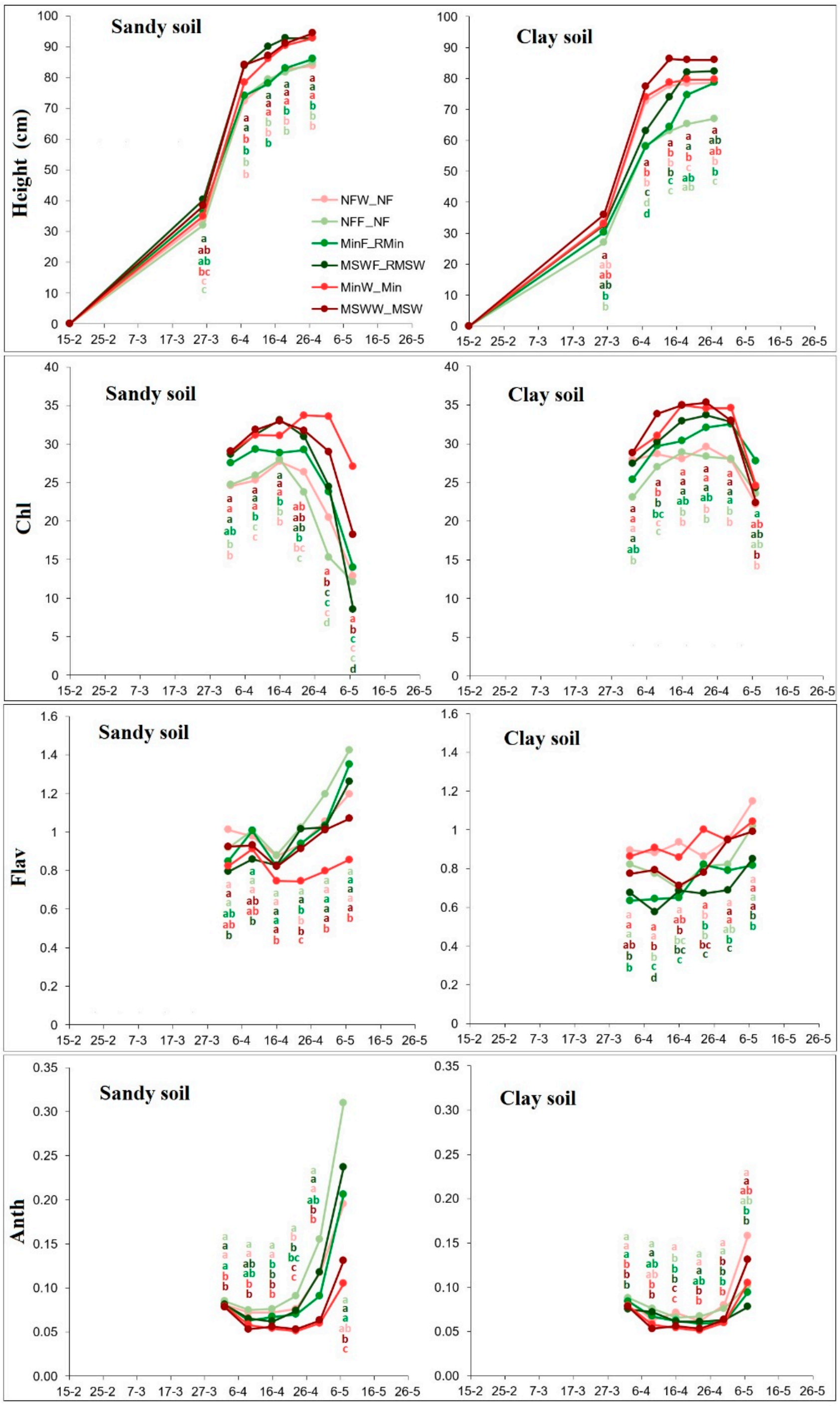

Figure 1. Effect of crop/fertilizer residual effect and present organic fertilization with bio-stabilized MSW amendment and mineral fertilization on buckwheat growth and pigment content (chlorophyll, Chl; flavonols, Flav; anthocyanins, Anth) under two different soils (clay and sandy) along the cropping season. Different letters for the same measurement and date represent differences among treatments ($p < 0.05$, Tukey HSD test). NFW_NF: unfertilized wheat as precedent crop and without BW fertilization; NFF_NF: unfertilized faba bean as precedent crop and without BW fertilization; MinF_RMin: residual mineral fertilized faba bean as precedent crop and without BW fertilization, only residual fertilizer effect; MSWF_RMSW: MSW fertilized faba bean as precedent crop and without BW fertilization, only residual fertilizer effect; MinW_Min: mineral fertilized wheat as precedent crop and with present mineral BW fertilization; MSWW_MSW: MSW fertilized wheat as precedent crop and with present MSW BW fertilization.

3.2. Previous Fertilization Residual Effect on BW Crop

The effect of the previous fertilization was analyzed among treatments NFF_NF, MinF_RMin, and MSWF_RMSW. All were previously cropped with faba bean and none received fertilizer during the present year; the only difference among them was the residual effect of the previous fertilization. In these treatments, the effect of the previous fertilization exhibited significant differences in biomass yield between the control without previous fertilization (NFF_NF), the residual mineral fertilizer (MinF_RMin), and the residual organic fertilizer (MSWF_RMSW) (Table 3). In sandy soil and clay soil, the previous application of MSW organic amendment exhibited, on average, 10% and 8% taller plants than with the residual mineral fertilizer, respectively (Figure 1). Higher chlorophyll values were obtained for organic residual fertilization and mineral residual fertilization compared to the control without previous fertilization for both soils. Organic residual fertilization presented higher chlorophyll content than mineral residual fertilization in both soils, with the exception of the final dates. For flavonol content, the control without previous fertilization showed the highest values in both soils, and more differences were observed between the organic residual fertilization and mineral residual fertilization in the clay soil than in the sandy soil. Less significant differences were obtained for anthocyanins in both soils between the organic residual fertilization and the mineral residual fertilization. In some cases, the anthocyanin content was influenced by the previous fertilization, obtaining higher values for the control without previous fertilization than the previously fertilized treatments. The residual effect of the fertilization influenced BW's biomass production with respect to the control without previous fertilization. In the sandy soil, significant differences were observed between the control and the residual mineral fertilizer. The same results were observed in the clay soil, even though the yield from the residual organic fertilizer was 22% higher than the residual mineral fertilizer. On the other hand, the residual fertilization effect did not significantly increase the BW seed yield, protein, and nitrogen content between previously fertilized treatments but increased these parameters in comparison with the treatment without previous fertilization. Additionally, some nutrients increased with the residual fertilization in both soils, such as copper, manganese, and zinc.

3.3. Fertilization System Effect on BW Crop

The effect of the fertilization system was analyzed in treatments NFW_NF, MinW_Min, and MSWW_RMSW. In this case, the precedent crop was the same (wheat) for all treatments, but they presented differences in the application of the same fertilizer source for two consecutive years. The direct application of mineral and organic fertilizers resulted in significantly taller BW plants than the control without fertilization in both soils. Although MSW organic amendment treatments obtained higher heights than the mineral treatments, these differences were, in general, not significant in the sandy soil (Figure 1). In contrast, the clay soil had significant differences between the fertilization systems, with the MSW treatments 8% taller than the mineral treatments. Chlorophyll content varied during the experiment, but in general, significant differences in both types of soils were observed between the control and the treatments with fertilization (mineral and organic). For the flavonol content, significant differences were observed throughout the experiment in both types of soil between the control, the mineral fertilization, and the organic fertilization. The highest values were observed for the control treatments without fertilization. Similarly, the anthocyanin content presented higher values for the control treatments, and significant differences were identified to occur between the control and the fertilized treatments. The direct application of fertilization in both types of soil significantly increased BW biomass production and seed yield with respect to the control (NFW_NF), but the type of fertilizer did not influence the biomass production or the seed yield (Table 3). On the other hand, the use of organic fertilizer increased the nitrogen and protein content compared to the control and mineral treatment in both types of soil. Other nutrients were also affected by the use of organic fertilizer in the clay and sandy soil, such as copper, iron, and manganese.

3.4. The Impact of the Cropping System on Soil Characteristics and Fertility

The effect of the residue from the previous crop was different in the two soils. It was found that the soil pH varied significantly in the sandy soil, but not in the clay soil in treatments NFW_NF and NFF_NF. While the E.C. was not affected by the residue of the previous crop, the organic matter in both soils presented higher values for the faba bean residue (NFF_NF) than for the wheat residue (NFW_NF), being 27% higher in both soils (Table 4). In general, the nutrient content in both soils and treatments did not significantly differ.

Table 4. Effect of organic fertilization with bio-stabilized MSW amendment and mineral fertilization on soil properties, soil nutrients, and heavy metals. Factors' effects over the measured variables were assessed as not significant (ns) or statistically significant (*) for $p < 0.05$ (mean values with different letters in the same row vary significantly).

Soil Properties	Soils	Treatments						Soil	Treatment	Soil × Treatment
		NFW_NF	NFF_NF	MinF_RMin	MSWF_RMSW	MinW_Min	MSWW_MSW	*p*	*p*	*p*
pH	Sandy	7.20 d	7.68 c	7.87 b	7.95 b	7.54 c	8.12 a	ns	*	ns
	Clay	7.77 b	7.74 b	7.83 b	7.99 b	7.89 b	8.20 a			
E.C. (dS/m)	Sandy	0.07 b	0.07 b	0.12 a	0.12 a	0.08 ab	0.11 ab	ns	*	ns
	Clay	0.10 ab	0.09 b	0.13 a	0.13 a	0.13 a	0.13 a			
Organic Matter (%)	Sandy	0.52 b	0.70 a	0.72 a	0.77 a	0.54 b	0.76 a	ns	*	ns
	Clay	0.52 b	0.71 a	0.74 a	0.76 a	0.62 b	0.84 a			
N Kjeldahl (%)	Sandy	0.07 b	0.09 ab	0.11 a	0.12 a	0.09 ab	0.12 a	ns	*	ns
	Clay	0.08 b	0.08 b	0.11 ab	0.12 a	0.10 ab	0.13 a			
P_2O_5 (g/kg)	Sandy	0.20 b	0.40 ab	0.70 a	0.80 a	0.50 ab	0.80 a	ns	*	ns
	Clay	0.40 b	0.30 b	0.60 ab	0.60 ab	0.60 ab	0.80 a			
K_2O (g/kg)	Sandy	1.60 b	2.10 b	1.90 b	4.60 a	4.20 a	5.00 a	ns	*	ns
	Clay	1.30 b	1.90 b	2.60 ab	3.20 ab	4.10 a	4.70 a			
CaO (g/kg)	Sandy	14.40 c	30.20 ab	35.40 a	36.10 a	22.80 b	24.70 b	ns	*	ns
	Clay	18.40 c	34.50 a	35.20 a	36.20 a	23.10 b	25.40 b			
MgO (g/kg)	Sandy	1.20 c	2.30 ab	3.40 a	3.60 a	2.70 ab	3.40 a	ns	*	ns
	Clay	1.50 c	2.80 ab	3.20 a	3.00 a	2.80 ab	3.50 a			
Zn (mg/kg)	Sandy	15.20 c	14.98 c	27.11 b	31.02 b	30.31 b	43.64 a	ns	*	ns
	Clay	18.89 c	18.03 c	26.21 b	33.26 b	32.10 b	49.78 a			
Cu (mg/kg)	Sandy	19.57 bc	17.56 c	21.06 bc	30.45 b	30.81 b	45.61 a	ns	*	ns
	Clay	18.54 c	15.00 c	20.36 bc	28.34 b	32.33 b	42.46 a			
Cr (mg/kg)	Sandy	5.93 c	4.96 c	16.04 b	20.06 b	27.23 a	36.37 a	ns	*	ns
	Clay	7.87 c	6.87 c	11.99 c	24.03 b	17.37 bc	39.62 a			
Ni (mg/kg)	Sandy	4.83 c	4.04 c	4.87 c	15.63 b	6.71 c	27.63 a	ns	*	ns
	Clay	4.77 c	4.03 c	5.10 c	15.98 b	6.43 c	27.56 a			
Pb, Cd (mg/kg)	Sandy	<0.20 a	<0.20 a	<0.20 a	<0.20 a	<0.20 a	<0.20 a	ns	ns	ns
	Clay	<0.20 a	<0.20 a	<0.20 a	<0.20 a	<0.20 a	<0.20 a			

NFW_NF: unfertilized wheat as precedent crop and without BW fertilization; NFF_NF: unfertilized faba bean as precedent crop and without BW fertilization; MinF_RMin: residual mineral fertilized faba bean as precedent crop and without BW fertilization, only residual fertilizer effect; MSWF_RMSW: MSW fertilized faba bean as precedent crop and without BW fertilization, only residual fertilizer effect; MinW_Min: mineral fertilized wheat as precedent crop and with present mineral BW fertilization; MSWW_MSW: MSW fertilized wheat as precedent crop and with present MSW BW fertilization. Heavy metals limits according to Spanish regulation (mg/kg dw) [42]: Cd = 3; Cu = 210; Ni = 112; Pb = 300; Zn = 450; Cr = 150.

The effect of the previous fertilization on both soils (analyzed in treatments NFF_NF and MinF_RMin and MSWF_RMSW) did not affect the soil pH, E.C., or the organic matter content in any soil. The only nutrients significantly influenced by the type of fertilizer residue were, in the sandy soil, potassium and nickel, and in the clay soil, nickel and calcium.

The effect of the fertilization system on both soils (analyzed in treatments NFW_NF and MinW_RMin and MSWW_RMSW) presented larger differences. In this case, the soil pH in the organic fertilization treatment presented higher values in both soils. For the E.C., no significant differences were found in the application of the organic fertilizer in both soils in comparison with the mineral fertilization. The organic matter content increased 29% in the sandy soil and 26% in the clay in the organic fertilization treatment compared to the mineral. Regarding the soil nutrient content, significant differences were observed between the control without fertilization (NFW_NF) and the fertilized treatments (MinW_RMin and MSWW_RMSW) in both soils. Some nutrients also exhibited variations between the mineral and organic fertilization treatments, such as zinc, copper, and nickel for sandy soil and zinc, copper, chrome, and nickel for clay soil.

4. Discussion

Buckwheat presented an interesting adaptation to the different situations studied, not only as a response to the soil properties and the nutrient availability but also to the precedent crop and nutrients residual content. It has been previously documented that adequate fertilization can enhance BW's biomass production [43]. The efficient management of fertilizers should be carried out not only to avoid nutrient leaching but also because providing an extra amount of nitrogen does not result in an increase in crops' seed performance and quality [40]. Although, when BW was fertilized, height was unaffected by the fertilizer type used (Figure 1), the values were in the range of the height reported in the literature [20], and some not significant tendencies to taller plants under MSW treatments were observed. A similar effect was observed for the crop yield. Fertilized treatments presented larger yields than non-fertilized ones, but there were no differences with respect to the fertilizer type used, although MSW tended to increase the yield in both soils (Table 3). In the same line, other authors observed BW yield increase after organic fertilization with manure compared to the control [7]. In relation to the nutritional status, it has been reported that nutrients from organic sources can be more efficient in protein synthesis than nutrients from mineral sources [44,45]. This effect can favor nitrogen content in seeds and can enhance seed production and quality. This effect can explain the higher nitrogen and protein content observed in BW seeds with organic fertilization in this experiment. Moreover, there was also an increase in the calcium, copper, iron, manganese, phosphorus, and zinc content after MSW fertilization than after mineral and unfertilized ones. These findings were consistent with previous investigations in which the application of organic fertilizers increased BW seed quality [46], in particular, the application of 60 Mg/ha of municipal waste compost achieved the highest seed protein in wheat [40]. All these differences in nutrient content between both fertilizer types were previously reflected in chlorophyll, flavonols, or anthocyanins along the crop cycle. BW fertilized with MSW usually presented larger chlorophyll values and lower flavonols than that fertilized with mineral fertilizer, and the differences with respect to unfertilized BW were even larger. In general, chlorophyll content can be used as an indicator of nitrogen deficiencies in crops [47], and flavonols and anthocyanins as indicators of abiotic stress [48,49]. Other authors have already identified at least two different responses to nutrient deficiencies in plants: (1) plants try to maintain their nutrient content, reducing their leaf size, such as the potato crop [50], and (2) plants that try to maintain their size, reducing their nutrient contents, such as many cereals [46]. In this case, BW seems to have responded in a similar way as cereals, presenting only differences in plant height under very poor soil conditions but a more gradual response to differences in leave pigments under different conditions.

In relation to BW's capacity to recycle the residual effect of the fertilizers from the previous cropping season, a significant influence of organic fertilization was seen at the starting phases of the experiment. BW height was around 8% taller after organic than after mineral fertilizer in both soils, and both were taller than the crop not previously fertilized. However, these differences decreased over time, and no final differences were observed between both previously fertilized treatments, although both were taller than the not previously fertilized one. A similar effect was observed with the yield, the protein content, and the rest of the nutrient contents, with the three residual fertilizer effect treatments statistically equal, although slight increases were observed for crops previously fertilized with MSW and previously fertilized with minerals compared to the not previously fertilized crop (Table 3). However, pigment estimation was again a very sensitive parameter for BW and was able to reflect, on many dates, the differences in nutrient availability due to previous fertilization residual effect, as observed by other authors for different crops [41,51]. However, the residual effect was not sufficient to provide the total nutrient necessities for BW potential growth, and differences were observed for all parameters of the fertilized treatments in both types of soils. As found in cereals, applying an optimal dose of organic fertilizer could improve BW seed yield and replace mineral fertilizers [52]. Although residual fertilization also increases to some extent seed yield, to obtain higher BW seed yields, direct fertilization is recommended, as the residual effects could decrease over time [53].

In relation to BW's capacity to recycle the residual nutrients from the previous crop, contrary to what was initially expected, the impact was not evident. There were some differences in pigment content and some nutrient concentrations at the end of the cycle, but none were consistent over time or according to soil type. There were also some increasing tendencies in crop yield and N content after faba bean, but they were not significant. Other authors have identified crops (i.e., many cereals) with a high potential to recycle residual nutrients from previous crops (mostly legumes) [54]. However, in this specific case of BW, the results were not clear. This result needs further confirmation under different conditions, but it might indicate some important facts. First, N liberation from the legume residue is not fast enough for a very short cycle, such as the BW crop cycle. Second, BW is not as dependent on N as on other nutrients (phosphorus, potassium, and calcium presented more constant ranges of concentration than N among treatments and soils). Finally, when planning a commercial crop rotation, it could be more interesting to include BW after a traditional over-fertilized crop (i.e., maize) than after a legume. BW seeds are able to germinate, emerge, and develop rapidly, making this crop not only an excellent suppressor of weeds and root pathogens [52,53] but also allowing it to enhance a fast uptaking of the already available nutrients present in the soil. However, this could be an inconvenience if the nutrients are released at a slower rate.

In this line, there was also the soil type impact. Clay soil had a significant impact on BW yield. But this impact was not the result of a larger availability of nutrients. Soil nutrient content was more related to the fertilizer type and schedule applied than to the soil type. The number of nutrients in the soil at the beginning and at the end of the experiment was not influenced by the soil type but by the treatment. In addition, with respect to the nutrients uptaken by the crop, only manganese presented larger concentrations in BW grown on clay soil (and a slight tendency in N concentration) than grown on sandy soils. Most of the largest nutrient concentrations in the plant were found in the crop grown on sandy soil, and only magnesium, potassium, and N presented no differences between soils. These findings are likely a result of the binding capacity of clay that fixates nutrients, making them initially unavailable for plant intake [55]. However, the fixed nutrients can become available for crop intake through soil changes, such as pH decrease [47], therefore not affecting the seed yield and quality as observed in this investigation. Moreover, the increase of BW yield grown on clay soil could be the response to the more stable water holding capacity or even nutrient distribution [51].

The fertilization treatments were also able to modify soil properties and soil nutrient availability for the BW crop. Soil pH in both soils increased due to the application of organic fertilization. At the start of the experiment, the pH was already above pH 7, which can be explained by the high content of CaO present in both types of soils. In some cases, the application of organic fertilizers led to a decrease in pH [56], but this is not the case with the MSW used here. Other authors have observed that BW acidified the soil to improve the extraction of nutrients from poor soils [57], but the soil used in our experiments presented adequate nutrient levels, which could be the explanation for why BW roots did not release acids. In other cases, as in this study, it has been reported that a soil pH increase could result from the application of organic fertilizers [48,57]. The effect of soil pH increase could be beneficial to decrease heavy metal bioavailability and thus could reduce its content in BW seeds [49]. The opposite effect was observed by other authors under mineral fertilization, where the soil pH decreased with the application of NPK mineral fertilizer [48]. In our experiments, the use of mineral fertilizer and the bio-stabilized MSW amendment as organic fertilizer significantly increased the pH of both soils. If other fertilizers for BW cultivation were to be used, the combination of organic and chemical fertilizers could be a possible solution to increase crop yield, avoiding soil pH decline [58], although BW can tolerate soil acidity (pH as low as 5) [59]. Additionally, the E.C. of soils with organic fertilization also presented higher values than with mineral fertilization and control. However, these differences were insignificant with respect to mineral and organic fertilization in both soils. Ozlu and Kumar [60] also observed an increase in E.C. due to organic fertilization, but the organic fertilizer used was manure, which could explain the large difference between the E.C. with manure and the E.C. with mineral fertilizer, being 2.2 times higher. It is important to highlight that the E.C. values in all treatments were less than 0.8 dS/m, which is the safe threshold for BW growth [61].

Numerous authors have documented the positive effects of organic fertilizers on total organic carbon and organic matter, which are directly related to soil fertility [62,63]. In this study, the organic matter content was in line with the initial expectations derived from applying the MSW amendment. The organic matter content was significantly influenced by the use of the organic fertilizer not only after two consecutive cropping seasons but also just during the first one, as a residual effect. Noticeable differences between the mineral treatments and the organic treatments were observed in both types of soils. In addition, it has to be noted that the direct application during two consecutive years of the organic fertilizer resulted in 32% higher organic matter content than the control, while the residual organic effects increased the organic matter content by 9% compared to the control. In the present investigation, both types of soil benefitted from the application of organic fertilization, increasing the organic matter content; for the clay soil, the application of organic fertilization can protect the structured clay colloids and reduce the mineralization ratio [64]. Furthermore, the increase in organic matter is particularly beneficial for the application of this MSW amendment, which presents a high aluminum concentration, and at high concentrations, this component can present toxicity. However, the increased organic matter content in both types of soils favored organic ligands in the topsoil and kept the available aluminum low [65]. As well as the high organic matter content, the availability of this non-essential, potentially toxic element was also reduced by the increase in both soils' pH. In a similar way, even though organic fertilizers, such as this MSW amendment, contain high sulfur content, most of the sulfur is organically bound, and in some cases, only less than 30% is plant-available, thus not presenting toxicity for the crops [66].

Results also showed that the nitrogen content in both soils had a positive response to fertilization with respect to the control, but it was not appreciable in organic fertilization treatments in comparison to mineral fertilization treatments. External nitrogen supply through fertilizers could be more important in cereals than in other crops, such as leguminous crops that form nodules [67], in order to promote growth and higher yields. Furthermore, regardless of the type of crop, the input of organic matter improves the quality of Mediterranean soil, which in general is recognized to be poor [68].

In general, soil nutrients increased as a result of the use of fertilization, as expected [69,70]. Phosphorus, potassium, and magnesium presented significant effects after fertilization with respect to the control treatments in both soils. This effect was even larger when the fertilizers, MSW and/or mineral, were applied during two consecutive cropping seasons. As previously mentioned, nutrient content in clay soils can be higher due to nutrient fixation, but these nutrients may not be available for plant intake. Another important aspect of organic fertilization is the final heavy metal content in soils. A high concentration of heavy metals can pose risks of toxicity to plants, microorganisms, and soil fauna [71]. In this experiment, the heavy metal content significantly increased with organic fertilization and with organic residue compared to mineral and control treatments. This increase was cumulative and was then larger when MSW was applied during two consecutive cropping seasons. This effect has already been reported in the literature, stating that the application of organic fertilizers can cause the accumulation of trace metals and therefore soil pollution [72]. Nevertheless, the use of some types of mineral fertilizers can also increase the content of heavy metals in soils [73]. Analyzing the heavy metal content in both soils and both experiments, the values of zinc, copper, chromium, nickel, lead, and cadmium obtained were below the limits established by the regulation. It has to be noted that further investigations considering longer periods using this organic fertilizer have to be carried out to ensure heavy metals do not exceed the regulated limits [42]. Heavy metal accumulation in soils can be highly dependent on the source of the organic fertilizer. Similar Zn content as in our investigation was found in the soil after the application of sewage sludge, which was on average 47 mg/kg, while the Cu concentration was 13 mg/kg, which was lower than that found for both soils in our investigation after the application of the MSW amendment [74]. Additionally, the long-term application of organic fertilizers from animal waste did not pose toxicity risks [75] and can be a way of increasing beneficial taxa and nutrient content [73]. Furthermore, the application of compost was found to be effective in restoring heavy metal–contaminated soils for cultivation [76]. As seen in previous studies, by applying organic fertilizers, metal mobility and bioavailability can be reduced, thus reducing metal toxicity. This is due to the contribution of organic matter, which bounds with the heavy metals and reduces its availability to crops [77].

5. Conclusions

The application of the bio-stabilized MSW amendment as organic fertilizer can increase BW biomass production and height, obtaining comparable results to those obtained applying a mineral fertilizer. Furthermore, the nutritional status of BW seeds improved with the use of the bio-stabilized MSW amendment in comparison to the mineral and control treatments, increasing the N, protein, and nutrient content. In this study, BW showed a gradual response to differences in leaf pigments between treatments along the crop cycle. Regarding BW's capacity to recycle the residual effect of the fertilizers, the findings revealed that the residual effect from the bio-stabilized MSW amendment was not sufficient to provide the total nutrient necessities for BW's potential growth and biomass production. Therefore, in order to enhance BW crop performance, the direct application of an optimal dose for BW is recommended, and in the case of using BW in a crop rotation system, including BW after an over-fertilized crop could be a suitable option.

In addition, this investigation studied the soil type effect on BW. The results highlighted that the effect on BW was more related to the fertilization impact than to the soil type. The fertilization treatments were able to modify soil properties and nutrient availability for BW crops. Fertilized treatments improved soil nutrient content with respect to unfertilized treatments; in particular, the use of the bio-stabilized MSW amendment improved the content of soil organic matter after its application during two consecutive growing seasons and even after the first season. At the end of this study, heavy metal concentration did not exceed the regulated limits. In general, under very fertile conditions, such as fertilized clay soils, BW was able to increase yield and nutrient uptake. In addition, BW was able to respond to many precedent residual effects under low nutrient availability. Because of this, BW could be a very interesting crop for very different rotations and cropping systems. Future work could be directed towards the study of BW fertilization with this bio-stabilized MSW amendment on the field and even in a crop rotation system in a long-term investigation.

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