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Suitability of Volcanic Ash, Rice Husk Ash, Green Compost and Biochar as Amendments for a Mediterranean Alkaline Soil

José María De la Rosa [1,*], Sara María Pérez-Dalí [1], Paloma Campos [2], Águeda Sánchez-Martín [1], José Antonio González-Pérez [1] and Ana Zelia Miller [1]

[1] Instituto de Recursos Naturales y Agrobiología de Sevilla, Consejo Superior de Investigaciones Científicas (IRNAS-CSIC), Avenida Reina Mercedes 10, 41012 Sevilla, Spain
[2] Facultad de Química, Universidad de Sevilla, C/Profesor García González 1, 41012 Sevilla, Spain
* Correspondence: jmrosa@irnase.csic.es

Abstract: Today's agriculture has the challenge of ensuring food supply for a growing population while human activity has already deteriorated about 40% of the world's soils, reducing productive capacity and increasing reliance on mineral fertilizers. In this context, valorizing and recycling mineral and agricultural waste for use as substrates or soil supplements enhance a sustainable economy, as well as the development of activities focused on finishing the soil nutrients' cycle. Looking for an effective solution to the massive waste generation and to enhance the agronomic qualities of soils, this study investigates the agronomic impact of contrasting inorganic and organic materials such as green compost (GC), wood biochar (WB), rice husk ash (RA), and volcanic ash (VA) as amendments to an alkaline Luvisol under controlled conditions. In this sense, barley seeds were planted and grown in a greenhouse under controlled conditions for 60 days on a soil amended with the aforementioned materials. The amendments demonstrated appropriate attributes for improving soil agronomic properties, enhancing the soil's nutritional content with no effect on barley germination. The WB showed high aromaticity and abundance of refractory organic C. Both ash-rich amendments showed high P and K contents, which are important elements for plant development. The GC has high water retention capacity and an adequate C and N balance. Although the application of the amendments had no effect on barley yields, the plants from the ash-amended pots showed an increase of Photosystem II efficiency, indicative of a better physiological status. In terms of toxicological safety, the abundance of trace elements in soils and plants was investigated. All soils met the maximum allowable limits for these persistent pollutants. Nevertheless, longer-term tests on plants are required to determine the risk of Pb accumulation, particularly in soils amended with GC and compost-ash mixtures. The simultaneous combination of organic and inorganic amendments showed adequate agronomic attributes. WB analysis revealed its great recalcitrance and carbon sequestration potential.

Keywords: sustainable agriculture; soil amendment; agronomic residues; food safety; volcanic ash

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1. Introduction

Agriculture is one of the supports to ensure food supply and the economy of rural areas. The Food and Agriculture Organization (FAO) states that most of the required food production increases should be preferentially carried out by boosting productivity in fields already under cultivation [1]. Nevertheless, human activity has degraded nearly 40% of the world's soils [2] through intensive tilling, erosion, mining and industrial activities, and excessive chemical inputs. This has led to a decline in many indicators of soil health, including nitrogen (N) retention and use efficiency, carbon (C) sequestration, and water infiltration and retention [3]. Soil degradation refers to environmental processes that destroy soil structure, affect its fertility, and undermine water quality. In Spain, soil degradation is aggravated by adverse climatic factors and deficient agricultural practices that contribute to the loss of the most fertile soil horizons, requiring additional fertilizer inputs. In addition, in Southern Europe, most of the agricultural soils (>75%) show organic C contents lower than 2% [4], increasing the risk of desertification. In fact, more than 50% of cropland soils in Spain have an organic C content of less than 1.7% [5]. Another problem facing agriculture is the generation of a huge amount of organic waste. The valorization and recycling of mineral and agricultural waste for use as substrates or soil amendments promote the local and sustainable economy as well as the implementation of activities based on closing the soil nutrients' cycle.

Plant residues are widely used through their transformation into valuable soil amendments such as traditional composting [6] or the more recently developed pyrolysis process (biochar). Green compost increases the content of OM in the soil, improves physical properties (infiltration rate, water holding capacity, aeration, porosity, etc.), and enhances the population of soil microorganisms, increasing their biomass, activity and biodiversity [7,8]. Decomposition of compost releases high amounts of inorganic nutrients (i.e., N, P, K, Ca, and Mg) in a form that can be taken up by plant roots [7]. It is well known that biochars have a high porosity, water retention capacity, more than 50% C in aromatic forms, and when produced under appropriate conditions, are free of persistent pollutant contaminants [9]. Biochar used in agriculture should meet the quality and safety requirements specified by the European Biochar Certification [10]. Furthermore, a sustainable biochar production model uses waste biomass as feedstock and ensures the use of fuel gases generated during pyrolysis (syngas). Biochar has proven positive impacts on sequestering C, reducing greenhouse gas emissions, significantly contributing to the recovery of polluted soils and improving soil fertility when added to arable soils [11–13].

Pyroclastic rock and ashes formed by volcanic eruptions are also used in agriculture as inorganic mulch. The main elements contained in volcanic rocks are Si, Ca, Mg, Al, Fe, K, P, and S [14]. Therefore, fertilizing soils with volcanic ashes can provide a wide spectrum of macro- and micronutrients for proper plant growth [14]. In fact, silicon plays an important role in the life cycle of plants; it increases plant resistance to biotic and abiotic stress. Nevertheless, Shamsjuddin et al. [15] reported that the effects of the action of volcanic rocks are only visible after about 6 months from the application. Studies conducted in Malaysia on rice and cocoa cultivation showed that the use of grounded basalt along with organic fertilizer improved the fertility of Ultisols and Oxisols. Similarly, Ramos et al. [14] showed that the acidic environment favors the release of mineral components from volcanic rocks; hence it is advisable to use them together with organic fertilizers such as compost. Nonetheless, studies concerning the effect of volcanic ashes on neutral-to-alkaline soils are scarce. The recent eruption of the Tajogaite volcano (La Palma Island, Spain) emitted 200×10^6 m^3 of pyroclasts [16,17] during 85 days since 19 September 2021, which occupied 1200 ha at the central-west part of La Palma Island, destroying 300 ha of arable lands. Consequently, it is of great importance to discern the potential agronomic application of this material, which is currently worthless.

FAO estimated a world rice production of over 750×10^6 tons in 2018 [18], while only Spain produced over 2.8×10^6 tons. Thus, rice husk is a very abundant agricultural residue. This material is usually used as a poultry bed or burned to generate energy. The remaining rice husk ash has been also applied as ameliorant for andosols causing increases in silica, anions concentration, cation exchange capacity and pH [19]. However, there is no information on the effects of the application of rice husk ash in alkaline soils poor in organic carbon.

There is no doubt that inorganic and organic waste own a high potential as raw material to mitigate problems that seriously affect the environment and agriculture in the Mediterranean Basin, such as soil loss due to erosion, lack of organic matter, and the need of mineral fertilizers. However, prior to the application of any soil amendment, safety has to be ensured by monitoring the abundance of non-biodegradable trace elements, including As, Ba, Cd, Cr, Li or Pb, classified as persistent toxic elements and that may result toxic for plants, animals and human [20,21]. Thus, in the absence of data on the application of these residual materials, alone or in combination, on Mediterranean calcareous agricultural soil, the primary goal of this research was to investigate the effects of a variety of organic and inorganic amendments derived from residues on the physical characteristics, composition, and growth of barley in a calcareous soil. To this end, this study characterized and tested the agronomic performance of organic amendments (wood biochar and green compost) and mineral amendments (volcanic ash and rice husk ash) on a typical Mediterranean soil (Luvisol). The effects of such contrasting amendments were investigated on plant germination and growth, and photosystem II (PSII) efficiency to reveal the impact of these amendments on plant health and food safety. Looking for an effective solution to the high amounts of waste generation and to the current challenges of sustainable agriculture, this manuscript provides valuable information for the assessment of the application of inorganic and organic materials, including green compost, wood biochar, rice husk ash and volcanic ash as amendments to alkaline soils of the Mediterranean basin.

2. Materials and Methods

2.1. Soil

The soil used in this study was collected in October 2021 at São Manços e São Vicente do Pigeiro site on coordinate of 38°27′23.5″ N; 7°41′40.2″ W, which is located at the center of the Alentejo region (Portugal). The climate of the area is dry-summer subtropical, often referred to as Mediterranean climate "Csa" with prolonged dry and warm summers. The average annual temperature and precipitation are 15.6 °C and 610 mm, respectively [22]. The soil was a Vertic Luvisol [23] with sandy clay loam texture and granite with abundant quartzite and calcite as soil parent material. This type of soil is usually employed for the cultivation of olive groves and rain-fed cereals, which are usual soils and crops in the South-West Iberian Peninsula. Afterwards, the sample was bulked, homogenized, dried at 25 °C for 48 h, sieved (<2 mm) and stored in a sealed box at 4 °C until analyses. The Luvisol has a total C content of 20.1 g kg^{-1} (11.1 g kg^{-1} Total Organic C; TOC), N content of 1.2 g kg^{-1}, alkaline pH (7.9), density of 1.4 g cm^{-3} and a water holding capacity (WHC) of 90% (Table 1).

Table 1. Physical properties and elemental composition of bulk soil and amendments.

	Soil	WB	GC	RA	VA
pH (H_2O)	7.9 ± 0.1	9.1 ± 0.1	6.3 ± 0.2	7.8 ± 0.0	6.0 ± 0.0
EC (µS cm^{-1})	147 ± 3	224 ± 3	440 ± 8	2005 ± 7	203 ± 2
WHC (%)	90 ± 2	159 ± 19	315 ± 61	467 ± 14	73 ± 4
Moisture (40 °C; %)	15.4 ± 0.2	5.8 ± 0.1	60.7 ± 0.9	3.2 ± 0.0	0.8 ± 0.1
Density (g cm^{-3})	1.4 ± 0.3	0.3 ± 0.0	0.3 ± 0.0	0.2 ± 0.0	1.2 ± 0.0
Ash (g kg^{-1})	944 ± 2	52 ± 4	570 ± 47	820 ± 1	1000 ± 3
TC (g kg^{-1})	20.1 ± 0.5	834.0 ± 2.0	395.0 ± 2.0	176.5 ± 18.7	- -
TOC (g kg^{-1})	11.1 ± 0.2				- -
TN (g kg^{-1})	1.2 ± 0.1	2.2 ± 0.1	15.0 ± 0.2	1.4 ± 0.8	- -
C/N	9	379	26	126	-
P (g kg^{-1})	0.23 ± 0.06	0.45	1.15	3.75	3.02
P (% P_2O_5)	0.05 ± 0.01	0.10	0.26	0.86	0.69
K (g kg^{-1})	2.3 ± 0.4	1.7	6.1	5.8	13.4
K (% K_2O)	0.28 ± 0.05	0.21	0.74	0.70	1.61
Al	27,679 ± 1593	156	8906	105	57,503
As	7.7 ± 1.1				
B	9.2 ± 0.9	6.9	18.3	9.5	12.3
Ba	143.3 ± 23.0	30.0	39.0	9.1	304.1
Ca	4780 ± 1327	10,322	40,595	3787	41,503
Ca (% CaO)	0.7 ± 0.2	1.4	5.7	0.5	5.8
Cd	0.1 ± 0.0				
Co	8.6 ± 1.3	0.4	4.5	0.4	56.6
Cr	13.9 ± 3.5				
Cu	6.5 ± 1.5				
Fe	17,798 ± 2298	198	11,929	432	73,130
Li	-	0.2	7.2	0.2	7.9
Mg	6165 ± 1006	549	4411	1517	28,997
Mg (% MgO)	1.0 ± 0.2	0.1	0.7	0.3	4.8
Mn	336.6 ± 38.8	196.1	310.3	483.6	1189.1
Mo	0.1 ± 0.0	0.4	1.0	0.9	2.3
Na	387 ± 221	185	1012	321	23,053
Na (% Na_2O)	0.0 ± 0.0	0.0	0.1	0.0	2.3
Ni	10.8 ± 3.3				

Table 1. *Cont.*

	Soil			WB	GC	RA	VA
Pb	9.6	±	0.5				
S		-		140.5	1804.4	1519.3	400.5
Sr		-		25.3	84.0	13.7	719.0
V		-		0.5	19.7	0.2	217.5
Zn	40.3	±	4.9				

The abundance of nutrients and micronutrients is expressed in mg kg^{-1} (dry weight basis) except for those indicated; Given error is standard error (n = 3). Abundance of As, Cd, Cr, Cu, Ni, Pb and Zn of the amendments are shown in Table 2.

2.2. Description of the Organic and Inorganic Amendments

Wood biochar (WB): was produced from chips of poplar wood pyrolyzed in a fixed bed reactor after purging with N at room temperature of 25 °C. The residence time was 30 min at 520 °C. The produced WB stands out for its high pH (9.1), C content (834 g kg^{-1}), WHC (159%), and aromaticity (H/C$_{at}$ ratio = 0.4; Table 1).

Green Compost (GC): was commercial and purchased from Carrefour S.A. (Madrid, Spain). This compost is free of mineral nutrients and additives, and it is made from a mixture of plant pruning waste and chicken manure. The GC has pH of 6.3 ± 0.2, electrical conductivity (EC) of 440 ± 8 µS cm^{-1}, WHC of 315 ± 61%, ash content of 570 g kg^{-1}, and C and N contents of 149 ± 2 and 6.8 ± 0.2 g kg^{-1}, respectively (Table 1).

Rice husk ash (RA): was supplied by Ebro Foods S.A. (Madrid, Spain) and was the result from the combustion of rice husks at the San Juan de Aznalfarache Factory (Seville) used for the production of parboiled rice. The RA had a pH of 7.8, electrical conductivity of 2005 ± 7 µS cm^{-1}, ash content of 820 ± 1 g kg^{-1}, and total C and N contents of 176 ± 19 and 1.4 ± 0.8 g kg^{-1}, respectively. The RA stands out for its high WHC of 467 ± 14% (Table 1).

Volcanic ash (VA): is the principal solid emission of volcanic eruptions and consists of rock particles of less than 2 mm in size [24], though their diameter can be extremely variable. The material used in this study was spewed and sampled at the North flank (28°37′19″ N; 17°52′25″ W) during the recent eruption of the Tajogaite Volcano in La Palma Island, Spain. The lava erupted showed a bulk composition of high-alkali (7.2 to 8.9 wt.% Na_2O + K_2O) and low-silica contents (44.8–45.4 wt% SiO_2) and it has been mineralogy classified from tephrite (initial phases) to basanite (from day 20 and thereafter). Initial tephrite lavas have low MgO (∼6 wt.%) and elevated TiO_2 (∼4 wt.%). In contrast, basanites composition was ∼8 wt.% MgO; 3.7 wt.% TiO_2 [16]. VA shows a pH of 6.0, electrical conductivity of 203 ± 2 µS cm^{-1}, and WHC of 73% (Table 1).

2.3. Experimental Set-Up of Greenhouse Pot Experiment

A greenhouse experiment was conducted (maximum/minimum temperatures of 26/21 °C) to investigate the effects of the application of the organic and inorganic amendments on germination rates, soil and plant nutrients, soil physical agronomic properties and growth parameters of barley. The dosage used was 5% of WB, GC, RA and VA, and their combinations (WB + GC, RA + GC, VA + GC, VA + WB and RA + WB) with a dose of 2.5% for each amendment. A completely randomized design was used with four replications in pots of 1 L in volume. In addition, four pots of un-amended soil were placed in the greenhouse and used as control.

For each pot, 6 certified seeds of *Hordeum vulgare* (Todocultivo, Ciudad Real, Spain) were planted. Before sowing, seeds were soaked in deionized water for 48 h. Soil water content was adjusted to 50% of soil water holding capacity (WHC) with dechlorinated water and maintained throughout the experiment. The plants were watered daily by weighing and using a moisture probe. The number of germinated seeds per pot was monitored regularly until 22 days after sowing (DAS). At day 22, 4 plants per pot were left to maintain the same number of plants per pot to avoid space as limiting factor for the development of the plants.

The efficiency of the photosystem II, determined as Quantum Yield (QYPSII), a stress-sensitive biochemical parameter, was determined at DAS 60 using a portable fluorometer (FluorPen FP-100; Photon System Instruments, Brno, Czech Republic). Determination of

QYPSII in light-adapted plants was calculated according to Maxwell and Johnson [25]. For each determination, three readings were measured from each leaf and averaged, 8 plants per treatment were measured.

Plant growth in the greenhouse was stopped after 60 days to avoid pot size becoming a limiting factor. Thus, the final destructive harvest was performed at DAS 60. The productivity is expressed as grams of fresh plant per pot. Harvested fresh plant samples were dried in an oven at 72 °C for three days to achieve a constant weight for dry yield. For the plant-to-root ratio, plants were uprooted from the pot and the roots were carefully separated and washed to remove the soil. The mean value of the weight of plant and root per plant was calculated by dividing the plant weight by the root dry weight.

2.4. Laboratory Analysis of Amendments, Plants and Soils

The pH, EC and WHC were measured as reported by Campos et al. [12]. Briefly, pH was measured with a Multimeter MM40 (CRISON Instruments, S.A, Barcelona, Spain) in the supernatant of a mixture prepared with the ratio 1:5 (w/v) sample:H_2O after 30 min shaking followed by 30 min of resting. EC was measured in the same solution after filtering. Soil moisture was elucidated by weighting after drying the sample at 40 °C and with a PMS710 soil moisture meter (Tsingtao Toky Instruments Co., Ltd., Qingdao, China). The WHC of amendments and soils was approached by the method by Campos et al. [12]. Total carbon (TC) and total nitrogen (TN) contents were obtained by dry combustion (1020 °C) using a Thermo Flash HT 2000 elemental analyzer (Thermo Instruments, Bremen, Germany). Germination rates per pot were calculated up to DAS 22. Stem height and soil moisture were monitored throughout the experiment. On DAS 60 of the experiment, the plants were cut, and the roots carefully separated by hand from the soil. The fresh and dry weight (72 °C; 72 h) of roots and shoots were determined. Aliquots of each original amendment and of the incubated soils were subjected to digestion in *aqua regia* (1:3 v/v of HNO_3:HCl; Sigma-Aldrich, Burlington, MA, USA), whereas plants were digested in ultrapure HNO_3 (Sigma-Aldrich, Burlington, MA, USA). Digestion was performed at 110 °C during 2 h in a DigiPREP digester block (SPS Science, Quebec, QC, Canada). Subsequent elemental analysis (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sr, V and Zn) of the filtered extracts was performed by inductively coupled plasma optical emission spectrophotometry (ICP-OES; Varian Inc., ICP 720-ES, Palo Alto, CA, USA). Blank solutions containing the HNO_3:HCl mixture and ultrapure HNO_3 (Sigma-Aldrich, Burlington, MA, USA) were also prepared following the same digestion procedure used for the samples and diluted up to 50 mL with deionized water. A certified reference material, Buffalo Lake Sediment (SRM 2704), from National Institute of Standard Technology (NIST), was analyzed to validate the extraction procedure.

Kjeldahl N content was determined in the soils after the greenhouse experiment by the method as described in Sparks et al. [26]. For comparative purposes, aerial biomass to root biomass ratios were also determined for each treatment.

The chemicals used in this study were of analytical reagent grade and ultra-pure water (Millipore, Direct purifier system, Merck, Germany) was used throughout the experiments. All polypropylene volumetric flasks used were previously pre-cleaned with 10% nitric acid, rinsed with deionized water and ultrapure water. The measurement of each of the parameters described above on pure soil and amendments were performed in triplicate (n = 3), while analyses on soils and plants after the pot experiment were performed in quadruplicate (n = 4).

2.5. Thermal Analysis of Amendments

Thermo-gravimetric analysis of amendments was conducted to discern the abundance of labile and recalcitrant organic matter using Discovery series SDT 650 simultaneous DSC/TGA instrument (T.A. Instruments Inc.,New Castle, DE, USA) under a N_2 flow rate of 50 mL min^{-1}. Samples (5 mg) were placed in Alumina cups and heated from 50 to 850 °C at a heating rate of 20 °C min^{-1}. The TG, dTG curves and mass loss were obtained via TRIOS software (T.A. Instruments, New castle, DE, USA).

2.6. Statistical Analysis

One-way ANOVA and Tukey's Honestly Significant Difference (HSD) test were performed after testing the normality (Shapiro-Wilk test) and homoscedasticity (Levene test) of the data. For non-normal variables, the differences between treatments were studied using the Kruskal-Wallis test and the Mann-Whitney U test. The IBM SPSS Statistics 26.0 software (SPSS, Chicago, IL, USA) was used for performing all statistical analyses using a significant level of $p = 0.05$.

3. Results and Discussion

3.1. Physiochemical Properties of Agronomic Interest and Elemental Composition of Amendments and Bulk Soil

The analysis of the composition and properties of the amendments showed great variability, as resulting from their different nature (Table 1). The WB shows an alkaline pH, the greatest C content, whereas EC and WHC are suitable for its use as an amendment. In relation to the nutrients content, and abundance of 2.2 g kg^{-1} of N is acceptable, although undoubtedly poorly available due to the extremely high C/N ratio (379). Lehmann et al. [27] reported that biochar addition without fertilizers causes the immobilization of N due to the high biochar C/N ratio. Furthermore, the P and K contents of WB are the lowest of the four amendments tested. Other authors have previously described that although biochars from wood have appropriate physical properties for their use as soil amendments and to improve soil structure, nutrients are usually scarce and have poor nutrient release capacity when added to soil and therefore should be applied mixed with compost or other nutrient rich amendments [28,29].

The GC exhibited a pH of 6.3, high WHC and low density. As remarkable aspects, GC revealed a high content of some elements of agronomic interest such as Fe, S and especially K and N.

The RA has a pH of 7.8, the highest WHC of all amendments (467%), the lowest density (0.2 g cm^{-3}), whereas its C and N content were 176 g kg^{-1} and 1.4 g kg^{-1}, respectively, which are in the mid-range compared to the other amendments. The most remarkable aspect in terms of nutrients composition of RA is the high P content, with 3.75 g kg^{-1}, which is similar to the amount reported by Bian et al. [30] for a rice husk biochar. This is due to the abundance of mineral ashes formed after the thermal decomposition of rice waste (ash content 820 g kg^{-1}), also responsible for its high EC reaching 2005 µS cm^{-1} (Table 1). The latter could negatively affect plant germination and development, especially in soils of Mediterranean regions affected by water deficit.

The VA had a slightly acid pH of 6.0, probably due to the condensation of strong mineral acids (primarily H_2SO_4 and HCl) in the cooling plume [31]. This inorganic amendment shows a high abundance of some macro and micronutrients of agronomic interest, such as K, P, Fe and Cu, whose content was as a whole higher than other similar samples previously published [32]. The abundance of K and P in VA is especially noteworthy, with 6 and 13 times, respectively, the concentration present in the soil. Consequently, VA could have additional interest due to its outstanding fertilizing capacity.

In addition to these major nutrients, such as N, P and K, which are necessary for many biochemical and physiological activities, certain trace elements designated as persistent hazardous elements, such as As, Ba, Cd, Cr, Li, or Pb, were also measured to assure the safety of each amendment (Table 1). The concentration of these elements in amendments needs to be kept below established safety limits to avoid health risks to consumers due to gradual accumulation in the body through consumption of food products cultivated in soils with high concentrations of these potentially toxic elements. Thus, Table 2 comprises the average concentrations obtained for these trace elements in the amendments, soils and harvested plants for each treatment, as well as the permissible maximum levels set by the

European Union [33] and the World Health Organization/Food and Agricultural Organization [34]. Concerning the amendments, the concentrations of As, Cd, Cr, Cu, Pb and Zn were always below the maximum allowable concentrations in soil ameliorants as established by the European regulations [20,21] and consequently, in terms of trace elements, it can be inferred that they are safe to use. Nevertheless, it should be stated that VA amendment has significantly greater concentrations of Cr, Cu, Ni, Pb, and Zn than the rest of the amendments. In any case, the concentrations of these persistent elements, excepting Ni, were substantially below the limit amounts stipulated by the EU, indicating that its application is safe. Heavy metal, together with mineral oils, is the most frequent contaminant in European soils [33]. Due to the higher mobility of heavy metals under acid conditions, organic and inorganic alkaline amendments are traditionally employed to bind the heavy metals in the soil and, therefore, reduce their toxicity [35]. Bearing in mind the stability, composition and alkalinity of WB and RA, these amendments should be strongly considered in future remediation trials of trace elements contaminated soils. Furthermore, for the toxic elements listed in Table 2, the WB also had the lowest significant quantities of any amendment.

Table 2. Average measured concentrations and maximum permissible values of toxic elements in amendments, soils and barley (or plants in the absence thereof) in mg kg^{-1}.

	Element	As	Cd	Cr	Cu	Ni	Pb	Zn
Amendments	Maximum permissible concentrations established by EU for amendments [19,20]	40	2	100 (OI); 150 (MM)	300 (OI); 600 (OMF)	50	120	800 (OF); 1500 (OMF)
	WB	0.8 ^{c}	<0.05 ^{b}	0.3 ^{c}	3.0 ^{c}	0.3 ^{c}	<1.0 ^{b}	5.0 ^{c}
	GC	7.0 ^{a}	0.1 ^{ab}	20.4 ^{b}	63.2 ^{b}	13.0 ^{b}	11.0 ^{a}	54.0 ^{b}
	RA	3.9 ^{b}	0.1 ^{ab}	0.7 ^{c}	5.9 ^{c}	0.8 ^{c}	<1.0 ^{b}	50.3 ^{b}
	VA	1.3 ^{c}	0.5 ^{a}	88.5 ^{a}	85.1 ^{a}	70.5 ^{a}	5.2 ^{a}	114.2 ^{a}
Soils	Maximum concentrations established for soils [36,37]	30 [1]	3	100	140	75	300	300
	C	11.7	0.3	42.7	7.5	6.2	1.6	60.0 ^{b}
	WB_5	9.8	0.1	37.8	6.9	5.4	3.1	53.3 ^{c}
	RA_5	9.7	0.3	39.3	7.3	6.0	2.4	86.9 ^{a}
	VA_5	13.1	0.2	42.3	8.2	6.6	2.9	92.4 ^{a}
	GC_5	11.1	0.2	43.0	16.1	7.5	3.4	79.7 ^{ab}
	WB + GC_2.5	9.3	0.2	40.5	10.4	6.2	2.5	88.1 ^{a}
	RA + GC_2.5	10.4	0.1	38.7	10.0	6.5	4.0	60.2 ^{b}
	VA + GC_2.5	8.1	0.2	39.9	10.8	7.7	2.4	58.1 ^{b}
	VA + WB_2.5	9.6	0.2	40.4	7.2	6.0	2.6	56.5 ^{b}
	RA + WB_2.5	9.8	0.2	40.6	7.7	6.4	5.4	57.7 ^{b}
Barley plants	Maximum concentration established by EU for food [38–40]	0.2	0.2	20	40	68	0.20 [2]	50 [2]
	C	b.d.l	b.d.l	1.9	5.2	b.d.l	b.d.l	31.8 ^{b}
	WB_5	b.d.l	b.d.l	1.7	4.6	1.0	b.d.l	21.6 ^{c}
	RA_5	b.d.l	b.d.l	2.3	5.1	b.d.l	b.d.l	52.9 ^{a}
	VA_5	b.d.l	b.d.l	2.3	5.2	b.d.l	b.d.l	55.6 ^{a}
	GC_5	b.d.l	b.d.l	2.4	5.0	1.4	1.2	34.0 ^{b}
	WB + GC_2.5	b.d.l	b.d.l	2.5	5.3	b.d.l	b.d.l	47.3 ^{a}
	RA + GC_2.5	b.d.l	b.d.l	2.3	4.8	1.4	1.4	28.1 ^{b}
	VA + GC_2.5	b.d.l	b.d.l	2.5	5.3	1.3	1.0	27.5 ^{b}
	VA + WB_2.5	b.d.l.	b.d.l	1.8	5.2	b.d.l	b.d.l	25.2 ^{bc}
	RA + WB_2.5	b.d.l	b.d.l	1.1	4.6	b.d.l	b.d.l	21.9 ^{c}

EU: European Union; WB: Wood biochar; GC: Green compost; RA: Rice ash; VA: Volcanic ash; C: Control; OI: organic improver; OF: organic fertilizer; OMF: organic mineral fertilizer; MM: mineral growing media; b.d.l: Below detection limit; [1] Recommended value; [2] Value established on wet matter; Where no letter is indicated there is no significant difference. Each type of sample (amendment, soil or plant) has been considered separately ($p < 0.05$).

3.2. Composition and Stability of Amendments by Thermal Analyses

Figure 1 depicts the TG curves of the amendments. The results of curve integration can be found in Supplementary Table S1. The derivative of weight loss (dTG; TG^{-1}), shown as a red line, allowed different regions in the amendments to be distinguished, representing different degrees of thermal oxidation resistance [41], and revealed their diverse nature. The WB is composed only of OM that decomposes at temperatures above 400 °C, with a maximum at 600 °C. More than 50% of the WB decomposes only at temperatures above 625 °C (Table S2) stating the abundance of polyphenols derived from lignin and condensed aromatic compounds [41]. As a result, WB has a high stability and potential for use in soil C sequestration [10]. The GC is formed by OM that decomposes at temperatures from 175 to 500 °C, with two well-differentiated blocks being dominated by the intermediate OM fraction with a relative abundance over 48% (Table S2) and a decomposition peak around 340 °C, which is usually attributed to the thermal disintegration of cellulose and hemicellulose, typically present in plant remains [42]. The RA sample has little intermediate OM, with 0.9% of the total weight, representing about 11% of the relative weight lost (Table S1) but it contains abundant recalcitrant OM (relative abundance of W2 = 23.7%) and stable OM combined with minerals (W3 = 41%; Table S1). Finally, the TG line (green) of VA is horizontal, implying that it is entirely composed of thermally stable minerals with no presence of organic compounds.

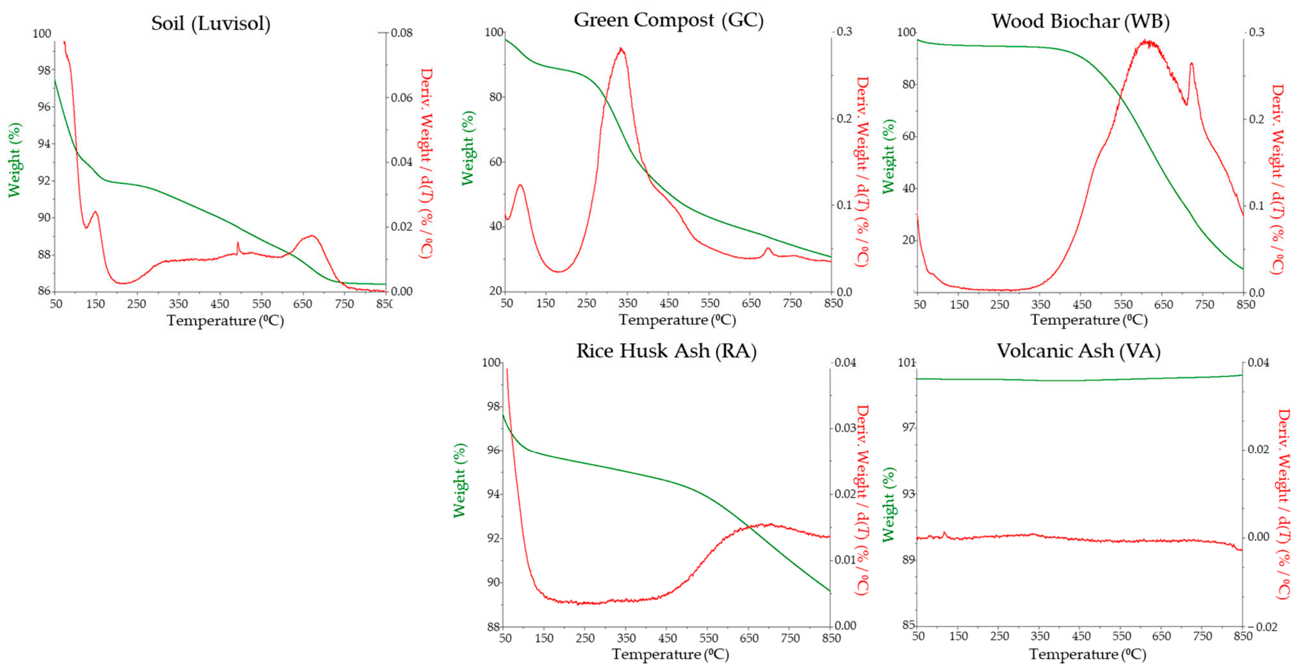

Figure 1. Thermo-gravimetric (TG) and derivative of thermo-gravimetric (DTG) curves of soil and amendments. Green lines are TGs, red lines are DTGs.

3.3. Effects of Amendment Addition on Soil Physical Properties and Composition

The effects of organic and inorganic amendments followed by 60 days of incubation on the physical characteristics and elemental composition of the Luvisol are shown in Table 3. Despite the fact that the amendments have a wide diverse of pH, ranging from the slightly acidic pH of VA and GC, with pH 6.0 and 6.3, respectively, to the alkalinity of WB, with a pH of 9.1, the soil pH remained at alkaline values close to the control (8.7), and only RA, RA + GC and RA + WB amended soils significantly reduced the pH to 8.3. This is owed to the alkaline nature of the soil used and driven by the strong buffering effect of the abundant carbonates. In addition, it has been reported that biochar derived from woody feedstock have a less prominent effect on soil pH compared with those derived from other feedstock [26]. The addition of 5% GC significantly increased the EC of the soils, ranging from 121 μS cm^{-1} (VA_5) to 183 μS cm^{-1} (GC_5). In all samples, these EC values are moderate, below 200 μS cm^{-1} and suitable for agronomic purposes.

Soil moisture at DAS 60 rose significantly in the pots treated with VA5, GC5, and the mixes WB + C2.5 and VA + GC2.5, exceeding 20%, compared to 13 to 15% recorded for the other treatments, including the control. Moisture retention in soil and water use by crops largely depends on pore size and particle-size distribution, which was governed by soil structure, texture, bulk density, OC content [43] and crop cultivated.

Table 3. Basic properties, elemental composition and macronutrients of soils after the greenhouse experiment (DAS 60).

	C	WB_5	RA_5	VA_5	GC_5	WB + GC_2.5	RA + GC_2.5	VA + GC_2.5	VA + WB_2.5	RA + WB_2.5
pH (H_2O)	8.7 ± 0.1 ^{ab}	8.8 ± 0.3 ^{ab}	8.3 ± 0.0 ^{a}	8.5 ± 0.2 ^{ab}	8.5 ± 0.0 ^{ab}	8.8 ± 0.1 ^{b}	8.3 ± 0.1 ^{a}	8.7 ± 0.1 ^{b}	8.4 ± 0.1 ^{ab}	8.3 ± 0.0 ^{a}
EC (μS cm^{-1})	127 ± 13 ^{b}	139 ± 19 ^{ab}	165 ± 9 ^{ab}	121 ± 3 ^{b}	183 ± 27 ^{a}	163 ± 18 ^{ab}	166 ± 21 ^{ab}	146 ± 37 ^{ab}	132 ± 16 ^{ab}	156 ± 5 ^{ab}
Moisture (%)	13.2 ± 0.1 ^{b}	14.7 ± 0.4 ^{b}	13.0 ± 1.9 ^{b}	20.0 ± 0.2 ^{a}	20.1 ± 0.3 ^{a}	20.1 ± 0.3 ^{a}	16.0 ± 0.9 ^{b}	20.1 ± 0.4 ^{a}	15.5 ± 0.9 ^{b}	14.2 ± 1.2 ^{b}
TOC (g kg^{-1})	9.0 ± 0.1 ^{a}	64.0 ± 13.7 ^{c}	25.0 ± 4.2 ^{b}	9.0 ± 2.1 ^{a}	26.0 ± 1.8 ^{b}	52.0 ± 5.7 ^{c}	27.0 ± 1.7 ^{b}	19.0 ± 5.3 ^{b}	30.0 ± 3.8 ^{b}	44.0 ± 13.5 ^{c}
TN (g kg^{-1})	1.10 ± 0.04 ^{de}	1.17 ± 0.03 ^{cd}	1.06 ± 0.01 ^{e}	0.94 ± 0.04 ^{f}	1.49 ± 0.02 ^{a}	1.23 ± 0.04 ^{bc}	1.30 ± 0.08 ^{b}	1.27 ± 0.08 ^{b}	1.13 ± 0.04 ^{de}	1.16 ± 0.05 ^{cd}
C/N	8	55	24	10	18	42	21	15	27	38
P (g kg^{-1})	0.63 ± 0.01 ^{efg}	0.59 ± 0.05 ^{g}	0.82 ± 0.02 ^{ab}	0.67 ± 0.01 ^{def}	0.85 ± 0.03 ^{a}	0.68 ± 0.00 ^{def}	0.76 ± 0.01 ^{bc}	0.69 ± 0.04 ^{cde}	0.61 ± 0.03 ^{fg}	0.74 ± 0.09 ^{cd}
P (% P_2O_5)	0.14 ± 0.00 ^{efg}	0.13 ± 0.01 ^{g}	0.19 ± 0.01 ^{ab}	0.15 ± 0.00 ^{def}	0.20 ± 0.01 ^{a}	0.16 ± 0.00 ^{def}	0.17 ± 0.00 ^{bc}	0.16 ± 0.01 ^{cde}	0.14 ± 0.01 ^{fg}	0.17 ± 0.02 ^{cd}
K (g kg^{-1})	4.01 ± 0.16 ^{abc}	3.67 ± 0.15 ^{cd}	4.22 ± 0.07 ^{ab}	4.16 ± 0.17 ^{ab}	4.40 ± 0.20 ^{a}	4.11 ± 0.08 ^{ab}	4.03 ± 0.11 ^{abc}	4.05 ± 0.30 ^{ab}	3.94 ± 0.01 ^{bc}	4.20 ± 0.40 ^{ab}
K (% K_2O)	0.48 ± 0.02 ^{abc}	0.44 ± 0.02 ^{cd}	0.51 ± 0.01 ^{ab}	0.50 ± 0.02 ^{ab}	0.53 ± 0.02 ^{a}	0.5 ± 0.01 ^{ab}	0.49 ± 0.01 ^{abc}	0.49 ± 0.04 ^{ab}	0.48 ± 0.00 ^{bc}	0.51 ± 0.05 ^{ab}

The given error is standard error (n = 4). Different letters indicate significant differences between treatments ($p < 0.05$).

The application of 5% of WB, WB + GC_2.5 and RA + WB_2.5, followed by VA + WB_2.5, GC_5, RA + GC_2.5 and RA_5 significantly increased ($p < 0.05$) the TOC contents of the soils (Table 3). Soil organic carbon has a beneficial effect on soil quality, fertility and stability, as well as agricultural production [44–47]. In addition, thermal analyses also indicate that most of this additional C incorporated to the soil due to the amendment with WB is highly stable (Figure 1), which is relevant in terms of C storage. Concerning the N content of the soils, it ranged between 0.94 and 1.49 g kg^{-1}. Soils amended with ash-based amendments displayed significantly less N compared to the rest. On the contrary, the application of GC to the soil, significantly boosted the abundance of N. Thus, the ratio C/N was modified after the application of the organic amendments being the highest for WB-amended soils, and similar to what has previously been published [47]. The C/N ratio is an important indicator of nutrient availability to plants because it describes the balance between energetic foods, represented by carbon, and protein-building material, represented by nitrogen [48]. A C/N ratio of around 24 is considered optimal to keep a high microbial activity. On the other hand, microbes in soils with a high C/N ratio (>80), must find additional N to balance out the excess C. This could result in a temporary N deficit (immobilization). To avoid yield, drag, crops with a high nitrogen requirement may need to be supplemented with additional N [49]. Therefore, higher doses of N-poor and C-rich organic amendments, such as WB, should not be applied. The application of RA, GC, RA + GC, and RA + WB significantly increased P contents as compared to the un-amended soil, which had a concentration of 0.63 g kg^{-1} (Table 3). The K content varied only slightly due to the addition of the amendments, and not significantly with respect to the control soils.

Concerning the presence of persistent toxic elements in soils, the concentrations of As, Cd, Cr, Cu, Ni, Pb, and Zn in soils were clearly below the maximum permissible limits in all cases (Table 2 and Table S2). The application of amendments did not lead to significant changes in the concentrations of As, Cd, Cr, Cu, Ni and Pb, according to statistical analysis of the data. This can be explained by the low concentration of these elements in the amendments and the relatively high background concentration in the studied soil. It should be emphasized that the soil was sampled within the Iberian Pyritic Belt (IPB), which has been exploited for metal mining for centuries. As compared to the control soil, Zn concentrations in soils treated with VA, WB + GC, and RA rose significantly.

Cr and Zn contents in all soils, including the control, reach 50% and 25% of permitted levels, respectively [36]. These concentrations are comparable to those found in agricultural soils reported in the Alentejo region and at the IPB by Galán et al. [50] and Pelica et al. [51], which advocate for soil monitoring, environmental control, and remediation in the region's soils. Nevertheless, total metal content of a soil usually provides unconfident information on the processes and dynamics of the availability and mobility of metals.

3.4. Effects of Amendments on Barley Plants Growth and Elemental Composition

The evolution of the number of germinated seeds is depicted in Figure 2. Germination rates for each treatment did not change over time (from DAS 9 to DAS 22). Nevertheless, germination rates were significantly lower in the VA + GC and VA treatments (67 to 75%) throughout the test, while it reached 100% in all other cases at DAS 22 but no noticeable changes in the average plant height were identified regardless of treatment and only the application of GC 5 significantly improved the average height by a few centimeters at the conclusion of the experiment (DAS 60; Table 4).

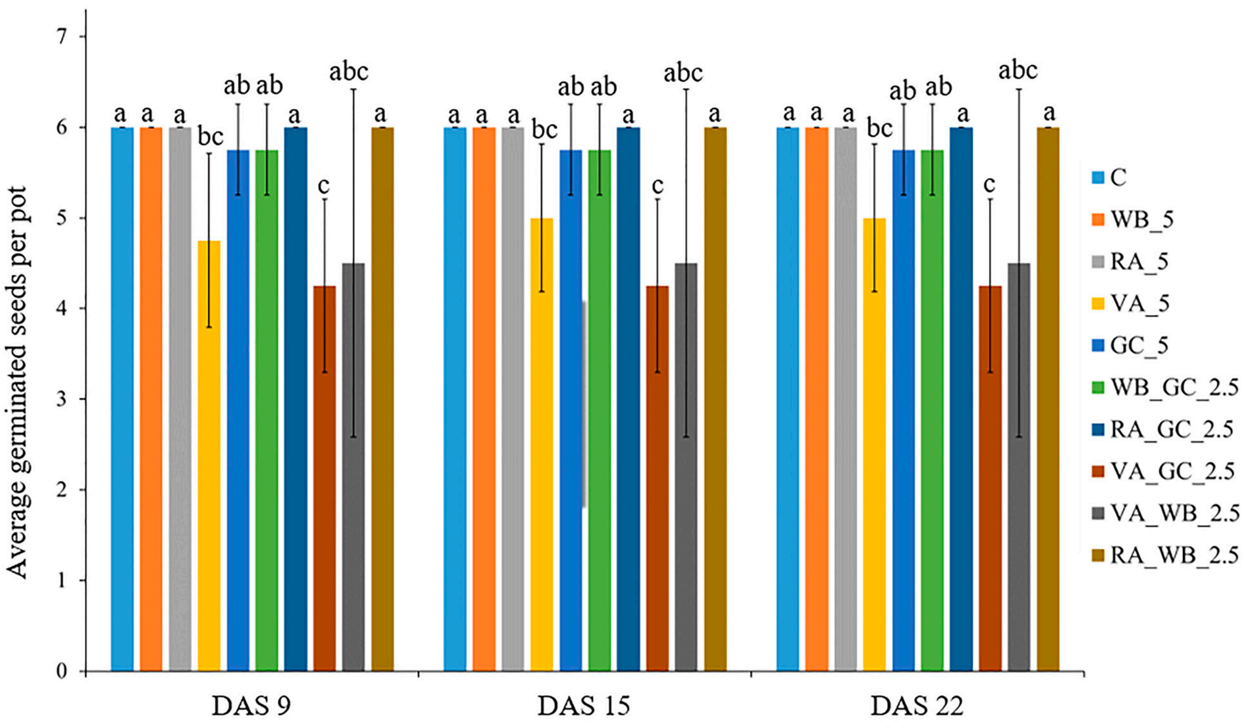

Figure 2. Average number of germinated seeds per pot up to 22 DAS. (means $n = 4 \pm$ standard error). Different letters indicate significant differences between treatments ($p < 0.05$).

Table 4 contains the information on plant growth characteristics such as height, fresh and dry weight of aerial biomass and roots, C, N, P, and K contents, and Quantum Yield (QY) at harvest. The application of RA + WB_5 caused the only significant improvement of the fresh weight (primary productivity) per plant, while in terms of dry biomass per pot the only significant increase occurred for treatment GC_5.

The QY is a well-known abiotic plant-stress marker that quantifies the Photosystem II (PSII) efficiency. A few studies previously assessed the effects of organic amendments on PSII in terms of QY [52–54]. In our case all the treatments produced values above 0.70, indicating the absence of plant stress. The plants of the pots amended with VA + GC_2.5, VA + WB_2.5 and RA + WB_2.5 increased PSII up to 0.79 pointing to the most suitable conditions. The C contents of the plants ranged from 382.5 g kg^{-1} (RA_5) to 399.0 g kg^{-1}

(WB + GC_2.5), whereas TN varied between 19.79 g kg^{-1} (RA + WB_2.5) and 26.78 g kg^{-1} (WB_5). These differences cannot be attributed to a specific trend, but rather to natural fluctuations inherent in plant variability and measurement error. In all the cases the N, P, K and Ca contents were greater than the minimum required in the feeding for ruminants and other herbivores [55].

The WB_5 and WB + GC_2.5 amendments produced the greatest root development with 4.5 and 4.9 g per pot (fresh weight basis), and therefore the lowest plant-to-root ratios (2.7 to 3.4 on fresh weight basis). This result is probably related to the high porosity and low density of these amendments. In contrast, the application of both types of ashes resulted in significantly decreased root development and the greatest plant-to-root ratios, implying improved water usage efficiency. This constraint is important and should be taken into account depending on soil texture, environmental conditions and crop type.

Table 4 and Table S2 also display the elemental composition of barley plants, including the main nutrients, after each amendment. The most abundant macro-nutrients were K > Na ≥ Ca ≥ P > S ≥ Mg in that order [56]. Plants grown in rich ash-amended soils (RA, VA, and their mixtures) depicted greater P proportions (around 5580 mg kg^{-1}) than plants grown in the pots with organic amendments without substantial distinctions. Potassium is responsible for many plant vital processes such as water and nutrient transportation, protein, starch synthesis and the process allowing plants to harness energy from the sun (photosynthesis), thus it plays an important role in the metabolic, physiological and biochemical functions of plants, being essential to increase the quantity and quality of yields [56].

Our results show that the fertilizer capacity of the amendments applied is rather medium to long term, which is consistent with their stable nature because the effectiveness of fertilization with volcanic rocks depends on the rate of dissolution of inorganic compounds contained in them [14] and therefore no major effects on productivity in a trial of only 2 months are expected. Jeffery et al. [57] in a comprehensive meta-analysis evaluating the impacts of biochar-amended soils on crop yield revealed that the greatest beneficial outcomes occurred on acidic sandy soils, whereas the results were predominantly neutral on fine-textured alkaline soils. This study reflects the still poor understanding of the relationship between soil organic matter and crop yield [58].

To assess the safety of organic and inorganic amendments for use in food production, the observed concentrations of As, Cd, Cr, Cu, Ni, Pb, and Zn in harvested barley from amended and control soils were determined (Table S2) and compared with the permissible maximum levels set by the European Union and World Health Organization/Food and Agricultural Organization (WHO/FAO) in Table 2.

As and Cd concentrations were lower than the detection limit (0.05 mg kg^{-1}) in all plants, and Cr, Cu, and Ni concentrations remained at least ten times lower than the maximum permissible concentration in all cases [38–40]. Pb concentrations in the barley collected in the GC amended pots and the compost mixtures with the two ash-rich amendments were found to be between 1.0 and 1.4 mg kg^{-1}, just below the maximum allowable limit given that the threshold was determined for fresh weight rather than dry weight [39]. Given that this is a persistent toxic element that accumulates in organisms, additional and longer-term trials applying these amendments are needed to ensure their safety. The concentration of Zn in the barley ranged from 21 to 56 mg kg^{-1} (Table S2). However, because it is determined on a dry weight rather than a fresh weight, as determined by the regulations on permissible limits for foodstuff [59], the Zn concentrations are at least 7 times lower than the authorized levels. Consequently, there are no immediate safety concerns with this element. Nonetheless, its long-term dynamics should be monitored.

Table 4. Growth parameters and elemental composition (C, N, P and K) of barley plants for each treatment.

	C	**WB_5**	**RA_5**	**VA_5**	**GC_5**	**WB + GC_2.5**	**RA + GC_2.5**	**VA + GC_2.5**	**VA + WB_2.5**	**RA + WB_2.5**
Height (DAS 60; cm)	54 ± 5 ^{b}	55 ± 4 ^{ab}	56 ± 3 ^{ab}	56 ± 5 ^{ab}	59 ± 2 ^{a}	57 ± 4 ^{ab}	57 ± 3 ^{ab}	57 ± 6 ^{ab}	57 ± 4 ^{ab}	54 ± 3 ^{b}
Quantum Yield (QY)	0.76 ± 0.02 ^{b}	0.75 ± 0.01 ^{b}	0.76 ± 0.01 ^{b}	0.75 ± 0.03 ^{b}	0.76 ± 0.01 ^{b}	0.76 ± 0.01 ^{b}	0.77 ± 0.03 ^{b}	0.79 ± 0.01 ^{a}	0.79 ± 0.01 ^{a}	0.79 ± 0.01 ^{a}
Fresh weight per pot (g)	14.7 ± 2.0 ^{ab}	12.2 ± 0.9 ^{a}	14.8 ± 4.3 ^{ab}	15.4 ± 4.2 ^{ab}	16.4 ± 1.8 ^{ab}	17.0 ± 4.1 ^{ab}	14.0 ± 2.2 ^{ab}	17.0 ± 3.7 ^{ab}	15.8 ± 1.4 ^{ab}	17.7 ± 1.2 ^{b}
Dry matter per pot (g)	2.0 ± 0.6 ^{cd}	2.4 ± 0.7 ^{bcd}	2.8 ± 1.1 ^{abc}	2.8 ± 0.9 ^{bc}	3.2 ± 0.5 ^{ab}	2.5 ± 0.4 ^{bc}	2.2 ± 0.7 ^{cd}	2.7 ± 0.5 ^{bc}	2.6 ± 0.5 ^{bc}	2.2 ± 0.3 ^{cd}
TC (g kg^{-1})	395.9 ± 3.2 ^{abc}	392.1 ± 1.6 ^{abc}	382.5 ± 3.1 ^{d}	388.5 ± 7.4 ^{cd}	397.6 ± 7.0 ^{ab}	399.0 ± 0.7 ^{a}	390.1 ± 2.5 ^{bc}	392.3 ± 2.6 ^{abc}	392.4 ± 1.7 ^{abc}	391.1 ± 4.6 ^{abc}
TN (g kg^{-1})	26.65 ± 1.42 ^{a}	26.78 ± 4.58 ^{a}	21.38 ± 1.77 ^{cd}	24.29 ± 1.97 ^{abc}	21.08 ± 1.93 ^{cd}	20.01 ± 1.44 ^{d}	20.60 ± 0.58 ^{cd}	22.66 ± 0.80 ^{bcd}	25.89 ± 1.66 ^{ab}	19.79 ± 1.18 ^{d}
P (g kg^{-1})	5.42 ± 0.08 ^{a}	5.07 ± 0.53 ^{abc}	5.55 ± 0.38 ^{a}	5.58 ± 0.39 ^{a}	4.72 ± 0.14 ^{bcd}	5.09 ± 0.20 ^{abc}	4.54 ± 0.42 ^{cd}	5.22 ± 0.42 ^{ab}	5.57 ± 0.21 ^{a}	4.24 ± 0.30 ^{d}
P (% P_2O_5)	1.24 ± 0.02 ^{a}	1.16 ± 0.12 ^{abc}	1.27 ± 0.09 ^{a}	1.28 ± 0.09 ^{a}	1.08 ± 0.03 ^{bcd}	1.17 ± 0.05 ^{abc}	1.04 ± 0.10 ^{cd}	1.20 ± 0.10 ^{ab}	1.28 ± 0.05 ^{a}	0.97 ± 0.07 ^{d}
K (g kg^{-1})	30.65 ± 2.77 ^{bcd}	33.00 ± 3.34 ^{ab}	35.65 ± 2.53 ^{a}	27.81 ± 0.55 ^{d}	31.51 ± 0.60 ^{bcd}	32.79 ± 0.14 ^{abc}	32.20 ± 2.30 ^{abc}	31.36 ± 2.95 ^{bcd}	31.24 ± 0.79 ^{bcd}	28.56 ± 1.38 ^{cd}
K (% K_2O)	3.69 ± 0.33 ^{bcd}	3.98 ± 0.40 ^{ab}	4.30 ± 0.30 ^{a}	3.35 ± 0.07 ^{d}	3.80 ± 0.07 ^{bcd}	3.95 ± 0.02 ^{abc}	3.88 ± 0.28	3.78 ± 0.35 ^{abc}	3.76 ± 0.09 ^{bcd}	3.44 ± 0.17 ^{cd}
Fresh weight per pot (g) *	3.9 ± 0.8 ^{bc}	4.5 ± 1.1 ^{ab}	2.4 ± 1.3 ^{d}	2.6 ± 1.2 ^{d}	3.0 ± 1.3 ^{cd}	4.9 ± 1.2 ^{a}	2.1 ± 0.7 ^{de}	3.7 ± 0.9 ^{bc}	3.1 ± 0.8 ^{cd}	3.1 ± 0.9 ^{cd}
Dry matter per pot (g) *	2.0 ± 0.7 ^{bc}	2.6 ± 0.5 ^{ab}	1.4 ± 0.8 ^{c}	1.3 ± 0.7 ^{c}	2.1 ± 0.8 ^{bc}	2.5 ± 0.6 ^{ab}	1.0 ± 0.5 ^{cd}	2.5 ± 0.6 ^{ab}	1.5 ± 0.6 ^{c}	2.1 ± 0.6 ^{bc}
Plant/root fresh matter	3.8	2.7	6.1	5.8	5.4	3.4	6.8	4.6	5.1	5.8

Given error is standard error (n = 4); * Measured values in roots. Different letters indicate significant differences between treatments ($p < 0.05$).

4. Conclusions

The composition and agronomically relevant attributes of contrasting organic amendments derived from residual biomasses and inorganic wastes, such as wood biochar, green compost, rice husk ash, and recent volcanic ash are described in this study. Despite the fact that all of the amendments demonstrated beneficial agronomic properties, such as low density of all organic amendments, the abundance of the nutrients P and K from the ashes, a high-water retention capacity, and adequate C/N balance of the green compost, the response of barley plants to the addition of these amendments to the alkaline Luvisol in almost all cases, neutral. This suggests that the experiment was probably too short for the barley plants to require the nutrients or acquire the possible advantages provided by these amendments. Similarly, the limited effect of the amendment application on the physical qualities of the Lluvisol is most likely owing to the high recalcitrance of all the amendments, excepting compost, along with the soil's buffering function, which would minimize the changes in such a short period of time. Pre-incubation or ageing of the amendments may be necessary if changes are to be observed in a short period of time. The concentrations of Pb measured in the barley plants at the green compost amended pots and its mixture with ashes were close to the maximum allowable limit for food, which suggests that longer-term research is required to ensure the safety of its use as soil amendment. The combination of an organic and an ash-based amendment appears to be the optimal choice based strictly on the composition and qualities of the pure amendments. According to the thermal study, wood biochar and volcanic ash are better suited for long-term effects and stability. Additionally, the wood biochar properties demonstrated a great potential for C sequestration. The use of residues in soil amendment reduces the environmental impact of waste management and thereby contributes to building a circular economy.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/agronomy13041097/s1, Table S1: Comparative thermogravimetry (TG) parameters in samples summarizing: Total weight loss for the temperature interval 50–850 °C (% ± 1%), weight losses and relative weight losses for the temperature intervals, 50–175 °C, 175–400 °C, 400–625 °C and 625-850 °C; Table S2: Micronutrient and heavy metal concentrations of soils and barley plants at DAS 60.

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Data Availability Statement: The samples and datasets of the current study are available from the corresponding author on reasonable request.

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Conflicts of Interest: The authors declare no conflict of interest.

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