Investigating the Suitability of Grape Husks Biochar, Municipal Solid Wastes Compost and Mixtures of Them for Agricultural Applications to Mediterranean Soils

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Abstract: Present work aimed at evaluating the leaching potential of grape husks biochar, municipal solid wastes compost and their combined application as amendments of sandy Mediterranean soil, in order to assess their capability of releasing/retaining nutrients or heavy metals and therefore their suitability for agricultural applications. Grape husks biochar was produced by pyrolysis at 500 °C in a fixed bed unit. Column leaching experiments, simulating Mediterranean rainfall conditions, were conducted. For all compost/biochar/soil combinations, alkali and alkaline earth metals showed greater solubility, increasing the pH of the extracts and thus decreasing the leachability of heavy metals Cr, Cu, Zr and Sr. Biochar co-application with compost did not prevent the leaching of nitrates, phosphates or trace elements; however, it did lower the chemical oxygen demand and allowed the slower release of sodium, calcium and magnesium from soil. As compared to compost, addition of biochar to soil increased the concentration of potassium by 76%, whereas it decreased that of heavy metals in the leachates by 40%–95%. Grape husks biochar could serve as a better soil amendment than municipal solid wastes compost and if carefully managed could be used as liming agent or fertilizer on acidic soils.

Keywords: amendment; biochar; compost; soil leaching

1. Introduction

The intensification of agricultural production to satisfy global needs has a negative impact on soil fertility, especially in regions with higher temperatures, such as Mediterranean. At the same time, large quantities of residues are generated, the management and disposal of which may create environmental problems. In Greece, about 4 million tons of agricultural waste from different crops (olive, grape, cereals, maize, cotton, etc.) is generated per year [1].

Compost produced from organic waste under aerobic conditions through mineralization and humification is commonly used to ameliorate the physical, physicochemical and biological properties of soils by increasing their organic carbon, replenishing various nutrients for plant growth, and saving fertilizers [2,3]. Aiming to reduce the amount of biodegradable wastes going to landfills, composting is often considered to be an environmentally friendly process. However, the degradation of organic compounds during composting can change the properties of waste biomass and increase the content of mobile forms of heavy metals, causing soil contamination [3,4]. This problem applies particularly to composts originating from municipal solid wastes (MSW). Furthermore, nutrient fluxes to the plants, especially nitrogen and phosphorous, should be carefully managed to avoid eutrophication or pollution of water sources [3].

On the other hand, recently, the production of biochar through biomass pyrolysis has gained increased attention as an alternative solution for recycling organic wastes which improve soil quality [5–8]. Additionally, during pyrolysis useful energy is extracted from the gaseous and liquid fractions of the process. This highly recalcitrant form of carbon has been found to contribute to carbon storage and sequestration by remaining in the soil for centuries, to increase soil fertility and remediate contamination by adsorption of pollutants [6–9]. The important properties of biochar as soil amendment are the surface area and porosity, the pH, the cation exchange capacity (CEC), the electrical conductivity (EC), the water holding capacity (WHC) and content of nutrients and heavy metals [6,8]. These are highly influenced by the type of feedstock used and pyrolysis conditions, especially temperature [5,8]. At higher temperatures, aromaticity, surface area, pH and mineralization increase, while nitrogen content and CEC usually decrease [7,10,11]. The primary mechanisms of nutrients availability such as nitrogen, phosphorous and potassium and heavy metals immobilization by biochar in soil include physical sorption and precipitation, complexation, ion exchange, electrostatic interactions or pH changes [7,10,12].

A lot of studies have been carried out to assess the benefits of using biochars produced from lignocellulosic biomass (woody residues, sugarcane straw, maize straw, rice husk) [4,6,12–16] or sewage sludge [9,17–19] for soil amelioration and remediation. Experimental equipment, conditions, application rates, different types of soil and the great variability of materials used, have all resulted in significant discrepancies in performance and agricultural utility [8,18]. Accordingly, there is a need for careful evaluation of each biochar for each specific site at lab level, prior to large-scale applications, in order to avoid expensive infrastructures and possible negative environmental effects.

The limitations induced by composts, especially those produced by sewage sludge or MSW, point to the investigation of the combined use of biochar and composts at various ratios, for potential improving retention capabilities of nutrients and toxic metals of soil systems. Such co-applications are limited in literature and are referred to co-composting of woody biochars with sewage sludge [4,20] or animal manures [2,21]. Furthermore, reports on utilization of biochar for soil amendment from solid wastes of wineries are scarce and limited to vine shoots or stalks [10,14]. Tropical soils of quite high acidity have been mostly used [2,4,9,12,13,15,16].

Based on this discussion, the present work is aimed at evaluating the leaching potential of grape husks biochar, municipal solid wastes (MSW) compost and their combined application as amendments of sandy Mediterranean soil, in order to determine their capability of releasing/retaining nutrients or heavy metals and therefore their suitability for agricultural applications. The experimental results obtained will enable the assessment of the biochar studied, or its co-application with compost as soil amendment.

2. Materials and Methods

2.1. Raw Materials and Characterization

A typical Mediterranean agricultural soil was selected for this work from the area of Agia-Chania in Crete (coordinates 35.4722° N, 23.9315° E). Systematic sampling was performed, according to the rectangular grid method, from the top 20 cm. The upper soil horizon sampling is a common practice in agronomical applications, when the effect of amendments or pollutants on crops is studied, or when soils/wastes are amended with additives prior to cultivation. After riffling, the soil was passed through a 2 mm sieve and analyzed for its proportions in sand, silt and clay by the hydrometer method [22]. The compost was provided by the local solid wastes management company DEDISA of the city of Chania. The biomass material for biochar production was grape husks, after extraction of juice, collected from a wine/spirit making factory. Following air drying, the material was ground in a cutting mill to a particle size <500 μm and riffled for obtaining representative samples.

Various modern analytical techniques were employed for the physical, chemical and mineralogical characterization of the solid materials tested, as well as for the analysis of water leachates. Structural

characteristics of the samples such as pore size, micropore volume and specific surface area were determined according to the BET method, using an automatic volumetric apparatus (Nova 2200, Quantachrome, FL, USA). Prior to analysis, the samples were out-gassed overnight at 110 °C under vacuum. Nitrogen adsorption at 77 K was applied at relative pressures of 0.03–0.35 during the tests. The water holding capacity was measured according to the method proposed by Ye et al. [23]. pH and electrical conductivity were measured in 1:5 solid to deionized water mixtures with a bench top meter precision pH/Ortmeter 920 and a Hanna bench conductivity EC215, respectively. Cation exchange capacity was determined by the ammonium acetate (NH_4OAC) extraction method [24]. A spectrophotometer (Spectrum 1000, Perkin Elmer, MA, USA) was employed for the Fourier-transform infrared spectroscopy (FTIR) analysis of the samples, in the range of 4000–400 cm^{-1} wavenumber, at a resolution of 4 cm^{-1}. The samples were pelletized after being mixed with KBr at a ratio of 1/100 w/w.

Proximate and ultimate analyses of soil, compost and biochar, for calculating the contents in volatile matter, fixed carbon, mineral matter and elemental C, H, N, S, O, were performed according to the European standards CEN/TC335. For ultimate analysis a CHNS analyzer (Flash 2000, Thermo Scientific, MA, USA) was used. Total organic matter (TOM) and total organic carbon (TOC) were measured by a thermal analyzer (TGA/DTG, Perkin Elmer, MA, USA), operated with a flow rate of air of 35 mL/min and a heating rate of 10 °C/min up to 900 °C and a Carbon analyzer (572-100, Gasometric, MO, USA), respectively.

Mineralogical analysis of samples was conducted by an X-ray diffractometer (D8 Advance, Bruker AXS, Karlsruhe, Germany), applying Cu Kα radiation and scanning range 2–70 2θ° with increments of 0.02°/s. For XRD spectra evaluation the software DIFFRAC plus Evaluation and the JCPDS database were used. Nutrient elements in all samples were identified using an X-ray fluorescence spectrometer (S2 Ranger/EDS, Bruker AXS, Karlsruhe, Germany) for major elements and an inductively coupled plasma mass spectrometer (ICP-MS 7500cx, Agilent Technologies, CA, USA) for trace elements, assisted by microwave digestion with HNO_3 acid in Anton Paar Multiwave 3000 oven.

2.2. Production of Biochar

Grape husks biochar was produced through pyrolysis experiments in a stainless steel fixed bed reactor (ID = 70 mm, H = 150 mm) heated by a furnace [8]. About 15 g of sample was placed onto a stainless-steel grid basket and inserted into the reactor. Once the unit was assembled, it was purged with nitrogen at a flow rate of 100 mL/min for 30 min, after which the furnace was heated up to 500 °C with a heating rate of 10 °C/min and it was hold at this temperature for 30 min. A Ni-Cr-Ni thermocouple was used for measuring sample temperature within the bed. Volatile products were passed through isopropanol ice-cooled baths for condensation of liquids. Following pyrolysis, the system was cooled under nitrogen and the resulting biochar was weighed and stored in airtight plastic vessels for further tests.

2.3. Leaching of Biochar/Compost Mixtures through Soil

In an effort to estimate the long-term leaching behaviour of the biochar, compost or biochar/compost mixtures through the soil, under the Mediterranean climate, prior to the tests the soil was thoroughly mixed with amendment materials at specific proportions in plastic pots (250 mL) and allowed to homogenize for one month in dark at about 25 °C. During this period, the pots were subjected to periodical wetting with de-ionized water and gentle stirring up. The amounts of grape husks biochar and compost used were 50 g/kg and 100–200 g/kg, selected to represent a high application rate on soils of 0–100 t/ha [25] and 0–200 t/ha, respectively [21]. The following mixtures were prepared: compost/soil (100 g/kg), compost/soil (200 g/kg), biochar/soil (50 g/kg), compost/biochar/soil (100 g/50 g/kg) and compost/biochar/soil (200 g/50 g/kg). All mixtures were air dried before being used for leaching experiments. The columns were made of PVC (ID = 2.5 cm, H = 25 cm) and were fitted with fiberglass and a valve with a stopper at the bottom, to control leachate collection. 100 g of each solid mixture was packed into the column, saturated with de-ionized water and drained (Figure 1).

Thereafter, each column was leached by percolation of purified water, with an amount (about 300 mL) which corresponded to the average annual quantity of rainfall in the area of Chania, Crete (~620 mm). The hydraulic head was kept constant during each test, on the basis of communicating vessels. Leaching was carried out in 3 steps over a 3-month period, in order to simulate local rainfall conditions. 100 mL of water was added in each column every month, between February and April 2019. Leachates were collected from each column over a period of 5 to 12 h, so that to get a better estimate of the time effect. Each effluent was filtered through a micropore membrane filter and the pH and EC of each extract were measured. Filtered leachates were kept in acid washed bottles in the refrigerator and prepared for the chemical analyses within a few days. Two experiments were conducted for each case and the values for each measured parameter were averaged (error was marginal ±2%).

Concentration of metals in the leachates was determined by the ICP-MS spectrometer, as discussed above. Chemical Oxygen Demand (COD) was determined according to the mercury digestion method 0077-SC, $N-NO_3$ according to the zinc reduction method 3689-SC, $P-PO_4$ according to the vanadomolybdophosphoric acid method 3655-SC and phenols content according to the aminoantipyrine method 3652-SC, using a UV-VIS spectrophotometer (Smart 3, LaMotte, MD, USA).
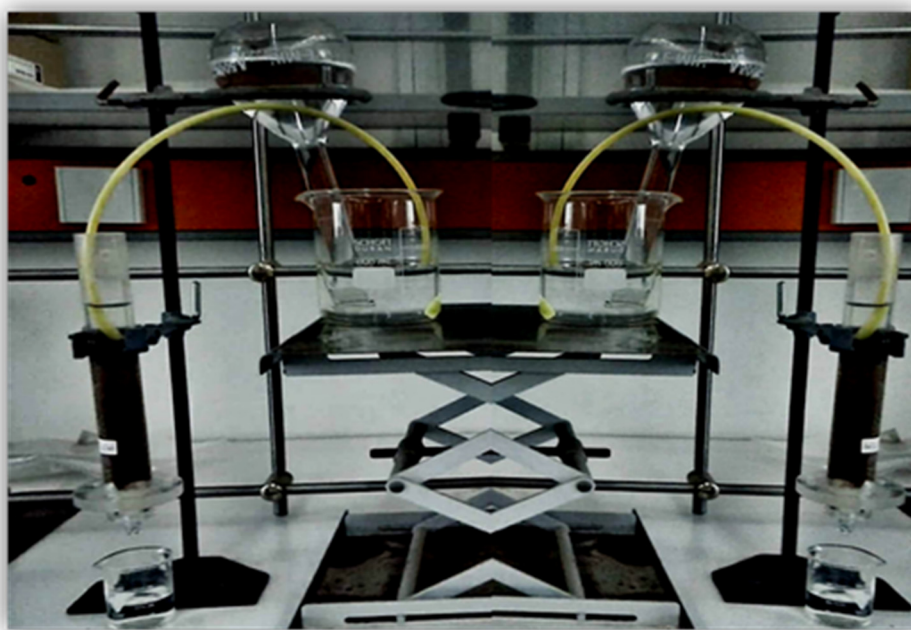

Figure 1. Experimental set up.

3. Results and Discussion

3.1. Physical and Chemical Properties of Solid Materials

The physicochemical properties of the solid materials under study are listed in Table 1. The pH of the soil and the compost was slightly alkaline, whereas that of biochar was highly alkaline due to the enrichment of grape husks with alkaline minerals, mainly carbonates of Ca, Mg and K (as shown below) after devolatilization. High pH is important for soil liming or use of biochars in agriculture, because it influences positively soil properties and leachability of metals including toxic elements from soils. The EC, a parameter used to estimate the amount of total dissolved salts in the sample, was very low in the case of soil in contrast to the compost and biochar values, which are considered high [7]. Excessive amounts of soluble salts in compost could decrease water uptake and nutrients by plants when applied to soils [4,26]. These properties are similar to those observed for other compost or biochar materials [4,7,15,26]. CEC indicates the ability of samples to adsorb cation nutrients that are essential for plants. Mineral soils generally have CEC less than 150 mmol/kg [16,26]. The soil used in

this study had a low CEC value (40 mmol/kg), due to its small percentage in clays, revealing that it had a reduced capacity for retaining cationic nutrient fertilizers. The high CEC of compost, as compared to literature data [5], indicates its ability for soil amendment. The grape husks biochar showed a CEC value within the range reported for biochars from different feedstocks [16,17,26].

As concerns the structural characteristics of the biochar studied, Table 1 shows that specific surface area and microporosity were quite low, most probably due to the high ash content, which could block the access of pyrolytic gas to the micropores. The average pore size indicates that the pores were mesopores and as such could improve aeration and water infiltration when applied to soils [8,18]. The latter is strengthened by the fact that the WHC of biochar was measured to be 1.1 g/g, while that of soil 0.26 g/g. Thus, water stored in mesopores could improve soil moisture retention and plant growth in case of soil/biochar mixtures.

Table 1. Physicochemical properties of solid materials.

Sample	pH	EC (mS/cm)	CEC (mmol/kg)	Pore Volume $\times 10^2$ (cm^3/g)	Average Pore Size (Å)	Specific Surface Area (m^2/g)	WHC (g/g)
Soil	8.2	0.05	40.0				0.26
Compost	7.7	6.5	653.9	0.19	54.1	0.8	
Biochar	9.7	15.3	205.2	0.12	45.3	0.9	1.1

The FTIR spectra of compost and grape husks biochar, representing the surface functional groups, are illustrated in Figure 2. The weak peaks of compost at 872 cm^{-1} and 1016 cm^{-1} were attributed to C=C and C-N stretching vibration of alkenes and amines, respectively. The peak at 1220 cm^{-1} of biochar indicates that various forms of oxygen during pyrolysis were transformed to C-O bonds representative of alkyl aryl ethers [27]. Furthermore, it could be associated with C-N bonds from amines. The broad bands at 1370 cm^{-1} for biochar and 1436 cm^{-1} for both materials correspond to the vibration of O-H groups from phenols and carboxylic acid, respectively. The weak peak of biochar at 1552 cm^{-1} is related to N-O bonding vibration from nitrocompounds. Moreover, the rather strong bands at 1666 cm^{-1} and 1670 cm^{-1} in both spectra can be assigned to C=C stretching of alkenes and to a smaller extent to C=N and C=O stretching of imines and conjugated ketones. Additionally, the sharp peaks at 2348 cm^{-1} and 2350 cm^{-1} are characteristic of O=C=O stretching from CO_2. The lower intensity peaks detected between 2850 cm^{-1} and 2950 cm^{-1} for both compost and biochar are ascribed to aliphatic C-H deforming vibration. Finally, the broad bands between 3400 cm^{-1} and 3750 cm^{-1} in these spectra indicate the presence of O-H groups of alcohols. Therefore, the FTIR results show that the surface of the materials under study was quite negatively charged, due to the hydroxylic and carboxylic groups, which could contribute to conjugation and cation bonding [17,28].

From the proximate and ultimate analysis results in Table 2, it can be observed that grape husks biochar had high fixed carbon content, almost twofold higher than that of compost, suggesting its stability to biological decomposition and importance for soil application requiring organic matter. The ash content ~30% is in the acceptable range of biochars for soil amendment [29]. Furthermore, the lower H/C and O/C molar ratios of biochar, as compared to compost, reveal its higher aromaticity and carbon stability [5,7], promoting carbon sequestration when added to soil. It has been reported that biochars with O/C molar ratios between 0.2 and 0.6 could have mean residence time in soil of 100–1000 years [30]. Present biochar fulfills the specifications for molar H/C and O/C ratios (<0.7 and <0.4, respectively) and for organic carbon content (>50% dry basis) established by EBC and IBI [31,32]. However, the higher N/C ratio of the compost with respect to biochar indicates its increased capacity for plant nutrition when incorporated into soils, thus favoring its use as soil amendment.
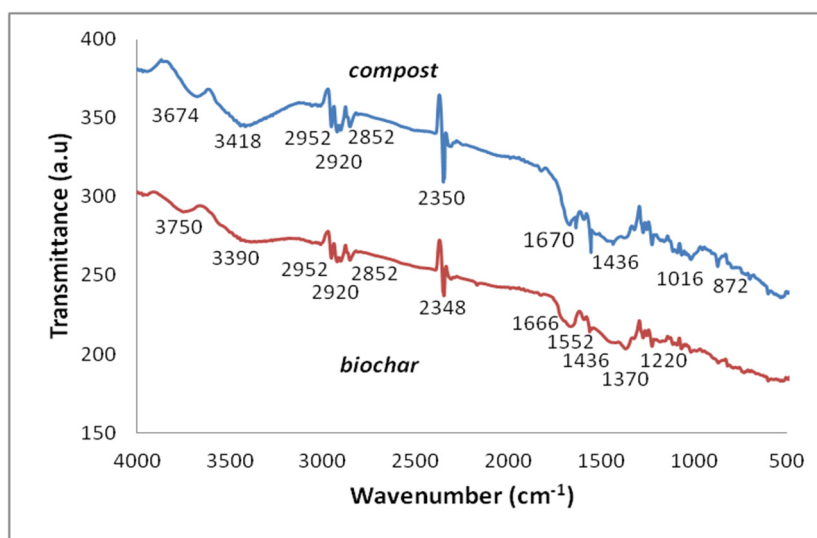
Figure 2. FTIR spectra of compost and biochar.

The XRD spectra of the solid materials under study are illustrated in Figure 3. The soil consisted mainly of quartz and to a smaller extent in muscovite and paragonite minerals, in accordance with the results obtained by the hydrometer method (sand 52%, silt 45%, clays 3%). The compost was very rich in calcite and also quartz. Potassium was mainly incorporated in sylvite and aphthitalite and in smaller amounts in microcline and muscovite. Phosphorous was present as hydroxyapatite. Grape husks biochar was dominated by calcium, as well as magnesium-based minerals in the forms of calcite, anhydrite, fairchildite, dolomite, magnesite and struvite. The speciation of potassium occurred in significant amounts as fairchildite, arcanite, sylvite and alite, while phosphorous was identified in hydroxyapatite and struvite. Small amounts of hematite and microcline were also detected.

With regard to the nutrient content, Figure 4 shows that the compost had higher concentrations of Ca and Mg than grape husks biochar. Nevertheless, the biochar studied was richer in these nutrients than other woody [6,15,21] or sewage sludge [17] biochars. Furthermore, it contained higher amounts of K and P as compared to compost, representing high rates of application [33]. K and P contents were similar or higher than other plant based biochars or biosolids [6,15,17]. However, the bioavailability of these nutrients in soils depends on the solubility of the various minerals containing these elements, as well as pores structure and size [11,15].

Table 2. Proximate and ultimate analysis of solid materials (% dry).

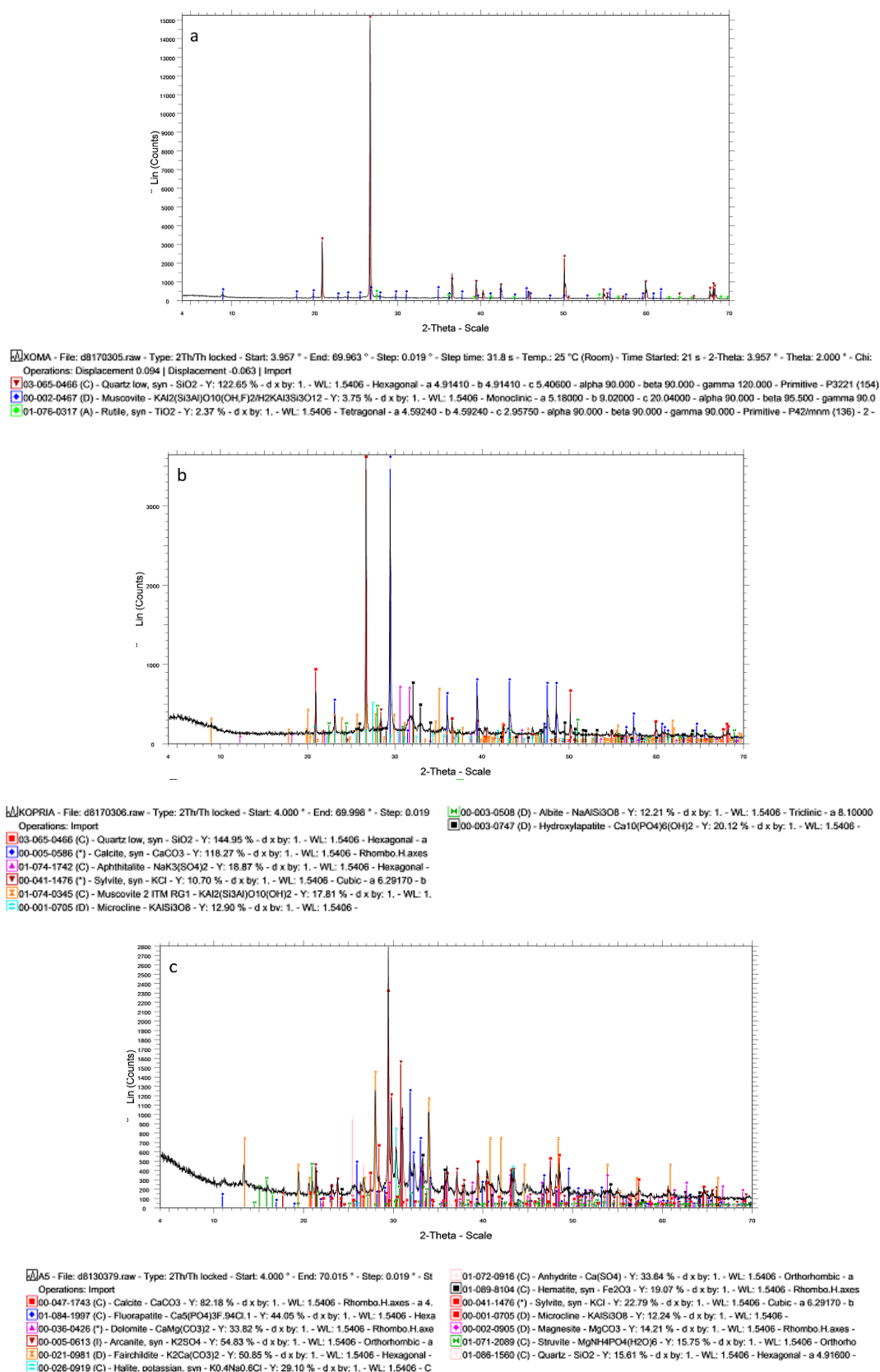| Sample	Soil	Compost	Biochar
Volatiles	1.3	22.7	30.9
Fixed carbon	0.9	26.9	38.7
TOM	2.2	49.6	69.6
Ash	97.8	50.4	30.4
C	0.25	24.7	56.2
H	0.16	2.6	1.8
N	0.04	3.0	3.1
O	1.7	13.7	8.1
S	-	0.38	0.4
TOC	0.01	4.2	56.2
H/C	7.6	1.26	0.38
O/C	5.4	0.41	0.11
N/C	0.15	0.10	0.05

Figure 3. XRD spectra of (**a**) soil, (**b**) compost ash, (**c**) biochar ash.

The heavy metal values of grape husks biochar were lower than the data reported in the literature for other biochars [9,17], apart from Zn the concentration, which varied depending on

feedstock [8,9,17,26]. Particularly, the levels of hazardous Cr, Pb and As were found to be much lower as compared to other studies [17,26,27] (Hg, Cd and Co concentrations were below detection limits). On the other hand, the compost which was produced from MSW, presented elevated amounts for most heavy metals and the contents of Cu, Zn and Pb were higher than other composted materials [4], but limit values for fertilization were not exceeded [34,35].
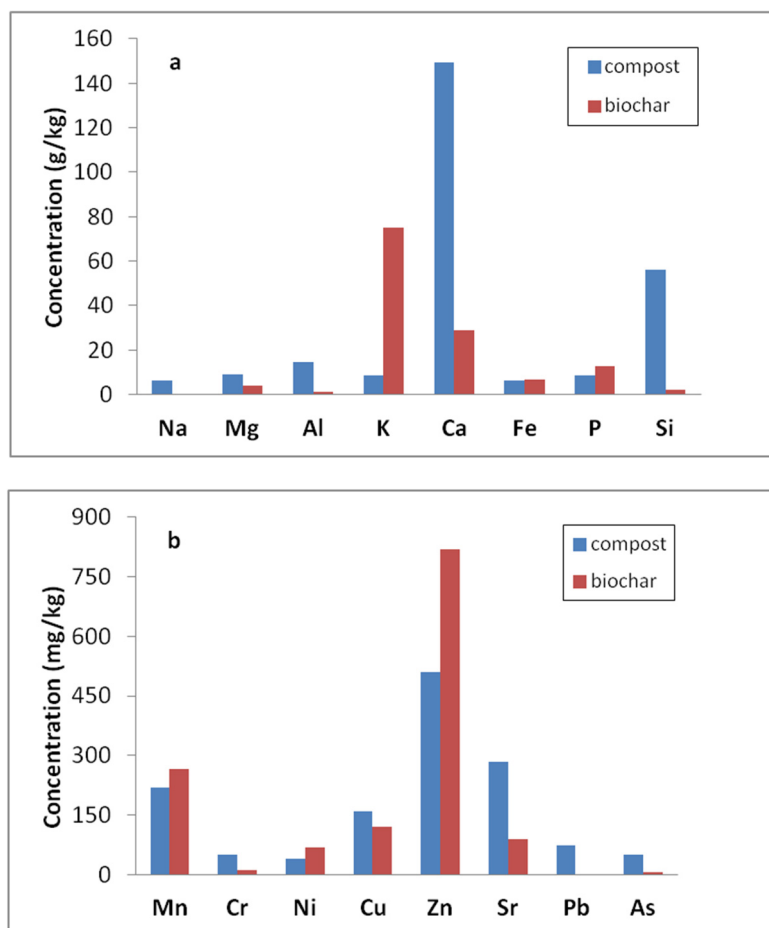

Figure 4. Concentration of ashes in (**a**) major and (**b**) trace elements.

3.2. Leachability of the Various Species from the Soil/Compost/Biochar Mixtures

3.2.1. Release of Phenols and Anions of Nitrogen and Phosphorous

The variation of pH with time, of the different leachates obtained from soil amended with compost, biochar or combination of these, is represented in Figure 5. As can be observed, in all cases pH increased from about 8 to 9 with time, revealing release of alkaline substances during the tests. The higher values obtained when biochar was added to the soil are attributed to its greater alkalinity, as previously shown (Table 1, Figures 3c and 4a). Similar results were obtained when the amount of compost was higher.

In contrast, as Figure 6 shows, the EC of water extracts decreased remarkably after collection of first leachate, implying that there were some readily soluble salts from soil mix, especially by incorporation of compost in the soil. Both pH and EC are known to affect the mobility and plant availability of nutrients, ions and trace metals [4,8,15,19].
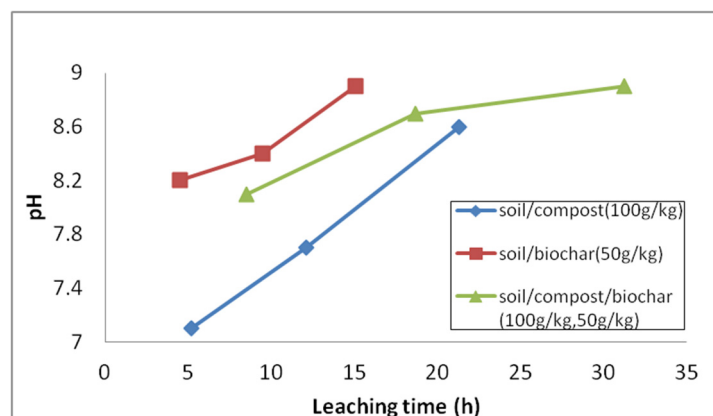
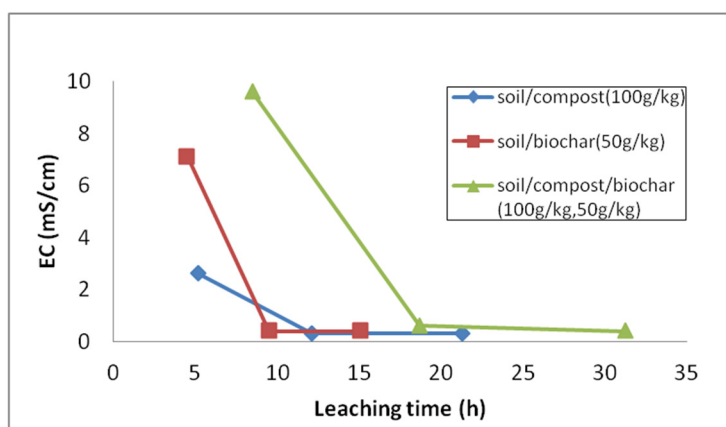**Figure 5.** Variation of leachates pH with time.

Figure 6. Variation of leachates electrical conductivity with time.

As concerns the chemical oxygen demand (COD), from Table 3 it can be noticed that the value corresponding to compost for the first leachate was not only higher than that of biochar, but also higher than other values reported for composts made from various wastes [28,36]. When biochar was added to the soil/compost mixture, the COD value was reduced, which could be related to the enrichment in oxygen-containing functional groups of grape husks biochar, as confirmed by the FTIR spectra previously discussed, that show an effective adsorbability for organic and inorganic matter in soil and water [28]. The same trend was observed for the amount of phenols extracted in water, which in all cases was low.

Table 3 shows that compost application to soil promoted nitrification, resulting in high concentrations of nitrate NO_3^- in water extracts. Furthermore, it can be noticed that biochar when added to the soil-compost mixture was not capable of retaining nitrate, which could most probably improve the nitrogen use efficiency as nutrient, according to previous investigations [13,18,19]. This behavior could be ascribed to the negative surface charges of biochar or compost, which—as FTIR analysis has shown—do not permit the adsorption, immobilization or ionic exchange of NO_3^- [37,38]. Furthermore, the low percentage of clays of the soil used did not favor the retention of nitrogen in soil [16]. Nevertheless, the amount of NO_3^- leached from biochar/soil was lower than that leached from the compost/soil.

As concerns regarding the amount of PO_4^{3-} in the leachates, present results show that there was no significant difference in the leaching of compost/soil (100 g/kg), as compared with the biochar/soil. However, more phosphorous leached from the compost-biochar/soil mix. As has also been supported by the work of other investigators [6,15], the extractability of PO_4^{3-} is mainly correlated to the mineral matter of biochars and pH-dependent reactions. In both compost and biochar phosphorous was

incorporated in hydroxyapatite. It is possible that, at the high pH measured during the tests, negative functional groups of compost or biochar (FTIR spectra) could adsorb cations of Ca and Mg, leading to the precipitation of Ca and Mg phosphates. These findings agree with some previous studies [6,39], while disagree with others [13,18,40], which have shown that biochar can sorb phosphorous reducing its leaching. Long-term experiments though, could demonstrate that fungi growing on biochar could capture phosphorous from its surface, allowing slow-release of phosphates for maintaining soil fertility and thus increase availability of phosphorous to plants [18].

Table 3. Leaching of phenols and anions of nitrogen and phosphorous from the soil/compost/ biochar mixtures.

Sample	Leaching Time (h)	COD (mg/L)	NO_3^- (mg/L)	PO_4^{3-} (mg/L)	Phenols (mg/L)
Soil/Compost (100 g/kg)	5.2	836	230	292	8.0
	7.0	101	-	98	4.8
	9.1	117	-	12	3.6
Soil/Compost (200 g/kg)	6.4	950	410	496	8.7
	8.0	240	-	326	5.1
	8.0	100	-	19	3.5
Soil/Biochar (50 g/kg)	4.5	677	170	259	3.0
	5.5	104	-	169	0.5
	5.0	26	-	14	0.4
Soil/Compost/Biochar (100 g/kg, 50 g/kg)	8.5	733	500	612	5.9
	10.2	106	-	230	3.9
	12.5	93	-	70	2.9
Soil/Compost/Biochar (200 g/kg, 50 g/kg)	9.3	806	705	614	6.1
	11.3	182	-	67	4.0
	11.5	84	-	57	2.8

3.2.2. Release of Metals and Trace Elements

Figure 7 illustrates the effect of compost, biochar and combined compost-biochar on the leaching behavior of alkali and alkaline earth cations Na, K and Ca with time. As can be seen, K and Na were extracted in higher amounts than Ca. These variations are partly due to differences in the solubility of the various compounds containing these elements, and partly due to differences in pore structure and size [15,19]. Sodium, which is a strongly hydrated cation, was quite mobile in soil containing compost. Furthermore, Ca, being rich in the form of calcite in compost, was considerably dissolved in water. The application of biochar to soil resulted in lower Na and Ca contents in the leachates and decreased their extractability in the presence of compost (the same effect was also observed for Mg, not shown in the graph). Such a decrease can be explained by the surface functional groups and micro-porosity of biochar, which could act as nutrient retention sites [19]. On the other hand, the high level of K in grape husks biochar in the soluble forms of sylvite, alite, arcanite and fairchildite, as shown in Figure 7, increased its concentration in the water extracts in all cases. Similar trends have been reported by other studies [8,13,15,19].

The cumulative concentrations of heavy metals in the leachates are represented in Table 4. Cd and Hg were not quantified in the extracts (their concentration was below ICP-MS detection limits). All values were below the European limits for soil leachates [31,41]. As can be seen, Cu, Zn, Mn and Sr were extracted in higher amounts from all soil mixture combinations. The total content of Cr, Cu, Zn and Sr leached upon biochar addition to soil was significantly reduced by about 73%–95%, as compared to compost, in agreement with previous studies [4,12,38]. The reduction of Mn was lower 7%–55%, whereas that of As and Pb was about 40% to 77%, implying that biochar lowers the risk of toxic metals uptake by water. The increased mobility of anionic As from soil/biochar, in relation to soil/compost mixtures, could be due to liming-induced deprotonation reactions, increasing negative charge on biochar surface [42].

Among the numerous factors affecting the leaching of trace elements from soils treated with compost or biochar, such as mineralogical and chemical compositions, various reaction kinetics, permeability and CEC, the high pH of present leachates, as previously shown, was a key factor for their low extractability and this is supported by many studies [2,4,12,13,18]. On the other hand, as Table 4 shows, combinations of biochar and compost were not beneficial in reducing heavy metals concentrations in water extracts and mobility, as opposed to some other investigations [4]. This effect was particularly pronounced for Cu and Zn. Various mechanisms have been proposed for retention of metals by biochars applied to soils, among which ion exchange or complexation, sorption, electrostatic attraction and competition between elements [12,38]. The present findings suggest that grape husks biochar did not interact with the compost used. As to the enhanced mobility of Cu and Zn in the presence of compost, it could be ascribed to the presence of humic acids in compost or increase in dissolved organic matter [2,10,21]. Finally, the higher levels of As and Pb in the leachates in the presence of compost in the soil/biochar mixture may pose phytotoxicity and risk to the environment in long-term applications.
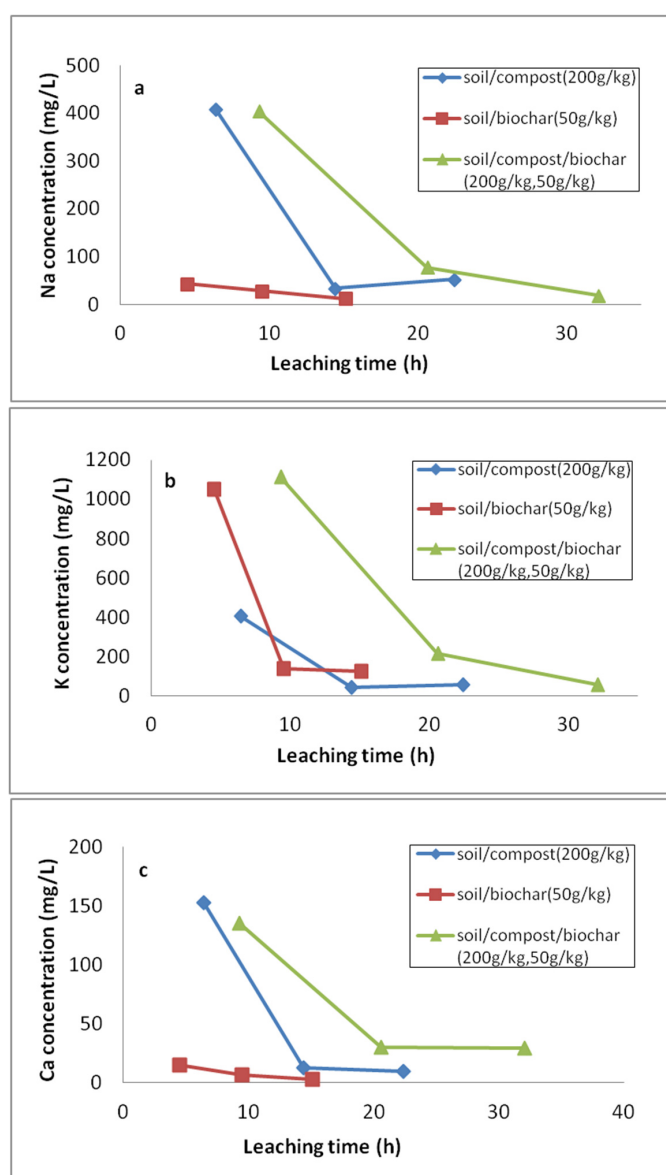

Figure 7. Concentration of leachates in (**a**) Na, (**b**) K, (**c**) Ca with time.

Table 4. Cumulative trace element concentrations (μg/kg) in the leachates and relative mass leached (%) *.

Sample	Cr	Mn	Co	Ni	Cu	Zn	As	Sr	Pb
Soil		0.45						111.3	
		(0.01)						(1.3)	
Soil/Compost	94.9	122.4	40.2	62.7	459.9	439.4	29.6	580.2	22.6
(100 g/kg)	(0.7)	(0.2)	(1.0)	(0.9)	(1.6)	(0.4)	(0.3)	(0.7)	(0.1)
Soil/Compost	98.0	245.3	61.0	183.1	1311.0	1730.2	25.0	828.3	59.6
(200 g/kg)	(0.5)	(0.3)	(1.3)	(1.1)	(2.0)	(0.8)	(0.2)	(0.6)	(0.2)
Soil/Biochar	26.4	113.6	98.3	181.2	67.0	113.4	17.3	100.0	13.6
(50 g/kg)	(0.4)	(0.1)	(3.1)	(1.7)	(0.3)	(0.1)	(1.7)	(0.2)	(0.3)
Soil/Compost/Biochar	188.1	884.2	93.0	601.3	6299.5	11395.2	55.5	610.9	439.2
(100g/kg, 50 g/kg)	(1.2)	(0.8)	(2.3)	(3.3)	(12.9)	(4.9)	(0.5)	(0.6)	(2.5)
Soil/Compost/Biochar	294.0	1480.1	140.7	971.9	8910.0	17367.3	37.0	114.1	820.9
(200 g/kg, 50 g/kg)	(1.2)	(1.0)	(2.8)	(3.7)	(11.8)	(5.2)	(0.3)	(0.8)	(2.6)

* Values in parenthesis represent cumulative mass leached (%).

4. Conclusions

The application of compost to soil promoted nitrification in the leachates (230–410 mg/L); however, at a lower rate, similar amounts of phosphates were extracted with biochar addition to soil (12–292 mg/L and 14–259 mg/L, respectively). COD and phenols concentration in solutions from compost/soil were higher than those of biochar/soil (COD 100–950 mg/L and 26–677 mg/L, respectively). For all compost/biochar/soil combinations, alkali and alkaline earth metal compounds showed greater solubility, increasing the pH of the extracts from about 8 to 9 and thus decreasing the leachability of heavy metals. For biochar/soil mixture the levels of Na, Ca and Mg were lower, whereas that of K higher, as compared to the compost/soil mixture. Furthermore, the concentration of heavy metals in the leachates upon biochar application to soil, was significantly reduced.

The combined application of compost and biochar to soil did not prevent the leaching of nitrates, phosphates or trace elements. This could be beneficial for N, P and micronutrients Cu and Zn-deficient soils. On the other hand, biochar co-application with the compost lowered the COD value and decreased the extractability of Na, Ca and Mg—allowing their slower release from the soil.

Overall, the present results suggest that grape husks biochar could serve as a better soil amendment than MSW compost and, if carefully managed, could be used as a liming agent or fertilizer on acidic soils. However, long-term field trials with specific biochar produced under different conditions and other soil types—including studying the impact on crops growth—are required to verify these findings.

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