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Evaluating co-application of horse manure and biochar mixtures for amelioration of Mediterranean soils

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***Abstract*—The aim of this study was to examine the feasibility of horse manure/grape skins-sewage sludge biochar co-application for amelioration of a Mediterranean type soil. Column leaching experiments were carried out simulating field conditions in South European countries. Raw materials were characterized by mineralogical and chemical analyses, whereas liquid effluents were analyzed for pH, electrical conductivity, chemical oxygen demand, nitrates, phosphates, phenols, nutrients and heavy metals. Application of grape skins or sewage sludge biochar, or horse manure to a quarzitic soil improved its water holding capacity, increased the pH, while reduced the electrical conductivity and chemical oxygen demand values of the leachates. Co-application of grape skins-sewage sludge biochar with horse manure allowed slower release of nitrates and Na, Ca and Mg elements from the soil, whereas higher release of K. Heavy metal levels in water effluents were very low. Those from soil/biochar mixtutres were about 40-80% lower than those from soil/manure blend.**

Keywords—soil; amelioration; horse manure; biochar; leaching

I. Introduction

Livestock manures are produced in huge quantities annually all over the world. Improper management, such as dunging outside processing industries or open dumping in rural areas, could result in environmental pollution. As an alternative to composting, which requires careful management in order to avoid eutrophication or contamination of soil with heavy metals [1-3] and increases production cost, land use of animal manures as fertilizers is the most common disposal method, widely accepted [4,5].

The limitations induced by composting, the relatively low fertilization potential of livestock manures and at the same time the large amount of waste biomass materials globally generated, led to the development of thermal treatment methods for these wastes to produce biochars. These carbonaceous materials, when applied at a proper rate to soil, have been proved to improve carbon sequestration [4], to reduce nutrient losses or heavy metals mobility during leaching [1,2,5], without compromising the microbial community composition [6] and remediate contaminated soil and water by adsorption of organic pollutants [3,7,8]. The important properties of biochars for soil amendment, such as the pH, the electrical conductivity, the water holding capacity, the surface area and structure and the content of organic and inorganic species, depend on the feedstocks used and thermal treatment conditions [3,4].

Most previous investigations, relevant to the exploitation of animal wastes, are referred to the combined utilization of woody biochars with composts to agricultural soils. Biochars of wood chips [9,10], rice husk [9], straw [7,11], empty palm fruit [11] and composts of pig manure [9,12], chicken manure [11], horse and rabbit manure [10] have been studied. The results, reporting retention of nutrients [11], immobilization of heavy metals [9], bioavailability of organic pollutants [12], microbial respiration or suppression of plant parasits [11], vary widely, due to the great diversity in raw materials and processing conditions, soil types and application rates [2,4,6,9,13]. On the other hand, there has been very little work on the co-application of untreated animal manures with biochars [5,6] and there is a need to investigate such effects for each specific site prior to large field trials, in order to identify the positive and/or negative consequences.

Based on the above, the aim of this study was to examine the feasibility of horse manure/grape skins-sewage sludge biochar co-application for amelioration of a Mediterranean type soil, through leaching experiments simulating field conditions in South European countries. Raw materials were characterized by mineralogical and chemical analyses, whereas liquid effluents were analyzed for pH, electrical conductivity, chemical oxygen demand, nitrates, phosphates, phenols, nutrients and heavy metals.

II. Materials and Methods

A. *Materials and Characterization*

The soil used in the experiments was sampled from the region of Akrotiri in Chania, according to the rectangular grid method, from the top 20 cm. It was riffled and sieved to a particle size < 2 mm. The horse manure was provided by a private company. Two biomass materials were used for the production of biochars, sewage sludge from the waste water treatment enterprise of the city of Chania and grape skins provided by a spirit making factory, in the area of Apokorona, Crete.

The biomass materials, after air drying, grinding to a particle size <500 μm (sewage sludge in a ball mill and grape skins in a cutting mill) and riffling, were pyrolyzed in a fixed bed system [3] up to 350°C. The heating rate was 10 °C/min, the nitrogen flow rate 150 mL/min and retention time at the final temperature 30 min.

Mineral phases in samples were detected by an X-ray diffractometer (XRD), model D8 Advance of Bruker AXS and identified through the use of JCPDS database and DIFFRAC plus software. Chemical analysis in major and trace elements was performed by an X-ray fluorescence spectrometer, model S2 Ranger/EDS of Bruker AXS and an inductively coupled plasma mass spectrometer, model ICP-MS 7500cx of Agilent Technologies, respectively.

B. Leaching Experiments

Horse manure and biochar materials were mixed with soil so that to represent common application rates of 0-100 t/ha [14], as follows: biochar/soil 50 g/kg, horse manure/soil 100 g/kg and biochar/horse manure/soil 50 g/100 g/kg. In order to simulate agronomic practices, these mixtures were subjected to an incubation procedure before the leaching tests. They were allowed to homogenize in glass pots in dark at about 25 °C for one month, applying periodical wetting and gentle stirring up. After this period, about 100 g of each mixture was packed into a PVC column (ID = 2.5 cm, H = 25 cm) fitted with fiberglass and a valve at the drain opening and saturated with de-ionized water. Leaching started by percolating de-ionized water through each column, while keeping the hydraulic head constant. In an effort to simulate local rainfall conditions in the region of Chania, Crete, the amount of water used corresponded to the average annual quantity of rainfall in recent years (~600 mm during 2015-2020) and the experiments were discontinuous over a period of three months. Liquid effluents were filtered through micropore membrane filters several times and kept in the refrigerator in acid washed bottles before analyses.

The Chemical Oxygen Demand (COD), nitrate ions N-NO_3, phosphate ions P-PO_4 and phenols of the leachates were analyzed by employing a UV-VIS spectrophotometer, model Smart 3 of LaMotte (methods mercury digestion 0077-SC, zinc reduction 3689-SC, vanadomolybdophosphoric acid 3655-SC and aminoantipyrine 3652-SC, respectively). The pH and electrical conductivity (EC) of the extracts were measured by a pH/meter model Toledo LE438 of Mettler and a conductivity meter EC215 of Hanna. The water holding capacity (WHC) of the samples before and after incubation was measured according to the method proposed by Ye et al. [15].

III. Results and Discussion

A. Mineralogical and Chemical Properties of Solid Materials

The mineral phases of the solid materials studied are indicated in Table 1. The principal constituent of the soil was quartz. Muscovite and chlorite were identified in smaller amounts. Horse manure was rich in quartz and whitlockite magnesian. Phosphorous was also incorporated in hydroxyapatite and graftonite. Potassium was bound mainly in sulfates and carbonates, such as aphthitalite, langbeinite and fairchildite. Sewage sludge biochar was dominated by whitlockite magnesian, calcite and hematite. Some iron was also detected in kennedyte, while phosphorous in fairchildite. Grape skins biochar was enriched in potassium-based minerals in the forms of arcanite, sylvite, fairchildite and microcline. A significant amount of calcium was also found in calcite, dolomite and anhydrite, whereas phosphorous was identified in fluorapatite and struvite.

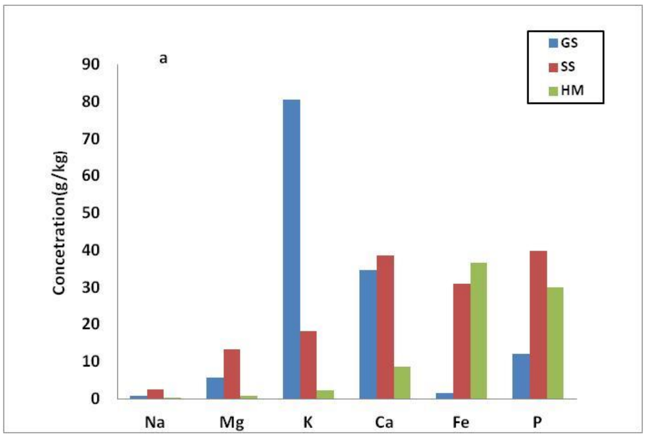
The concentrations of major and trace elements in the horse manure and the sewage sludge and grape skins biochars are compared in Fig. 1. As can be observed, both biochar materials were richer in nutrients content in comparison to horse manure, with

TABLE I. Mineralogical analysis of solid materials ashes

Mineral phases	Soil	Grape skins	Sewage sludge	Horse manure
Quartz SiO_2	+++	+	+	+++
Anhydrite $CaSO_4$		+	+	+
Halite NaCl		+		
Calcite $CaCO_3$		++	++	+
Microcline $K(Si_3Al)O_8$		+		
Fairchildite $K_2Ca(CO_3)_2$		+	+	+
Arcanite K_2SO_4		+++		
Hydroxyapatite $Ca_5(PO_4)_3(OH)$				+
Fluorapatite $Ca_5(PO_4)_3F$		+		
Magnesite $MgCO_3$		+		
Hematite Fe_2O_3		+	++	
Muscovite $KAl_2(Si_3Al)O_{10}(OH,F)_2/H_2KAl_3Si_3O_{12}$	+			+
Montmorillonite – Na-Mg-Al-Si_4O_{11}				+
Sylvite KCl		+		
Aphthitalite $K_3Na(SO_4)_2$				+
Struvite $MgNH_4PO_4(H_2O)_6$		+		
Dawsonite $NaAl(CO_3)(OH)_2$			+	
Kennedyite $Fe_{0.33}Ti_{0.52}Mn_{0.5}Ti_2O$			+	
Gmelinite $NaAl(SiO_3)_2.3H_2O$			+	
Whitlockite magnesian $Ca_{18}Mg_2H_2(PO_4)_{14}$			+++	++
Langbeinite $K_2Mg_2(SO_4)_3$				+
Graftonite $Fe_3(PO_4)_2$				+
Manganosite MnO				+
Dolomite $CaMg(CO_3)_2$		+		+
Clinochlore $(Mg,Fe)_5Al(Si_3Al)O_{10}(OH)_8$	+			

a. *+++: high intensity ++: medium intensity +: low intensity* the exception of iron. Sewage sludge biochar presented the highest concentrations in Ca, Mg and P, whereas grape skins biochar in K. These concentrations are similar or higher than those of other biochar materials previously reported [6,16], revealing that they could improve soil fertility upon application. However, this is governed by the solubility of the mineral phases incorporating the various nutrient elements [17]. As concerns the trace elements, from Fig. 1b it can be seen that both biochar samples contained elevated amounts of micronutrients Zn, Cu and Mn, whereas horse manure sample was particularly enriched in Mn. The levels of toxic heavy metals Cr and Pb of grape skins biochar were lower than those of horse manure material. Nevertheless, all measured values were below limit values for soil amendment [18]. Hazardous species Hg, Cd, Co and As were found to be below instruments' detection limits.

The water holding capacity of the soil and its admixtures with biochar, horse manure or biochar/horse manure, before and after incubation procedure, is illustrated in Fig. 2. It is clear that the water holding capacity of all blends increased after incubation, following the increase in samples volume. A better performance was observed for grape skins-sewage sludge biochar (70:30)/soil 50g/kg. This improvement implies retention of water by soil mixtures favoring plant growth.



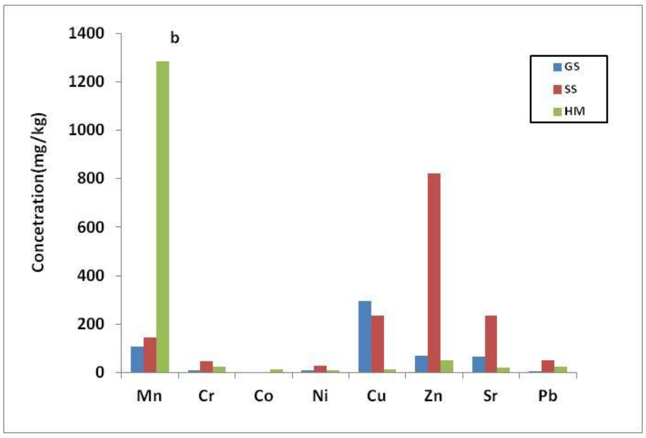


Fig 1. *Major (a) and trace (b) elements in biochars*

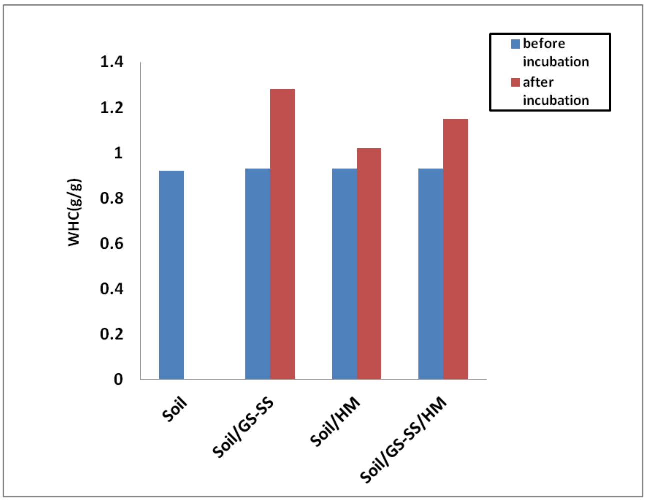


Fig 2. *Water holding capacity before and after incubation*

B. Leaching of Nitrogen and Phosphorous Anions and Phenols from Soil Mixtures

The variation of pH, electrical conductivity, nitrate ions, phosphate ions and phenols in the leachates of soil admixed with biochars, horse manure or combination of these, with time, during the whole period of three months, is represented in Table 2. In all cases pH increased gradually with time from about 7 to 8.2, due to the dissolution carbonates of Ca, Mg and K (Table 1) during the tests. The higher pH values corresponded to soil/biochar blends, which were more alkaline. In contrast, the electrical conductivity of water effluents decreased significantly after collection of the first leachate, in which some readily soluble salts were released, reaching nearly zero values at the end of three months period. It is known [2,3,19] that a higher pH and a lower electrical conductivity favor the availability of nutrients by plants.

Table 2 clearly shows that the concentration of nitrate ions in water extracts was similar for all soil mixtures and was distributed about equally during the whole leaching period. When grape skins-sewage sludge biochar was added to the soil/compost mixture, it can be observed that the amount of nitrates leached was lower, implying some adsorption on biochar surface, effect which could be positive for the efficient use of nitrogen by plants for nutrition [19,20].

In relevance to the phosphate ions, Table 2 indicates that these were not practically released in liquid effluents. This behavior can be explained by the mineralogical analysis of the materials studied (Table 1), which showed that phosphorous was mainly incorporated in insoluble phases, such as whitlockite magnesian. However, it has been found [20] that

TABLE II. LEACHING OF ANIONS AND PHENOLS FROM SOLID MIXTURES

Sample	Leaching time (days)	pH	EC (mS/cm)	NO_3^- (mg/L)	PO_4^{3-} (mg/L)	Phenols (mg/L)
Soil/GS	1	7.3	2.5	34	-	3.0
	8	7.5	2.0	32	-	
	22	7.7	1.3	30	-	
	36	8.0	1.0	29	-	
	60	8.1	0.7	25	-	
	90	8.1	0.4	22	-	
Soil/SS	1	7.0	0.7	34	-	0.64
	8	7.2	0.6	31	-	
	22	7.4	0.5	30	-	
	36	7.7	0.4	29	-	
	60	7.8	0.3	23	-	
	90	7.8	0.3	19	-	
Soil/GS-SS	1	7.3	0.7	26	-	2.1
	8	7.5	0.6	29	-	
	22	7.7	0.4	33	-	
	36	7.9	0.3	26	-	
	60	8.0	0.4	22	-	
	90	8.0	0.4	18	-	
Soil/HM	1	6.9	1.9	28	-	1.1
	8	7.0	1.6	29	-	
	22	7.2	1.0	29	-	
	36	7.4	0.7	31	-	
	60	7.6	0.5	24	-	
	90	7.7	0.4	19	3	
Soil/GS-SS/HM	1	7.0	1.7	27	2	2.9
	8	7.2	1.5	26	2	
	22	7.6	1.2	25	2	
	36	8.0	1.0	23	2	
	60	8.1	0.7	18	3	
	90	8.2	0.5	14	3	

TABLE III. CUMULATIVE CONCENTRATIONS OF MAJOR AND TRACE ELEMENTS IN THE LEACHATES

Sample	Soil/GS	Soil/SS	Soil/GS-SS	Soil/HM	Soil/GS-SS/HM
Major elements (mg/kg)					
Na	56.1	44.3	59.8	173.8	133.6
Mg	28.8	30.0	26.8	65.8	62.8
K	263.7	25.4	129.7	76.0	281.8
Ca	11.8	116.0	47.8	186.5	142.0
Fe	4.2	0.06	2.3	0.2	0.49
Trace elements (μg/kg)					
Ni	12.8	-	39.1	67.1	62.5
Zn	21.8	-	47.0	73.2	95.5
Sr	229.3	334.8	365.8	626.5	653.5

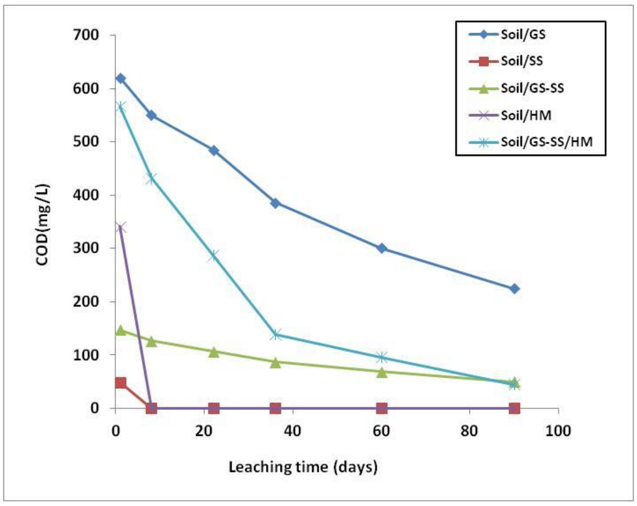


Fig 3. *Variation of chemical oxygen demand with time*

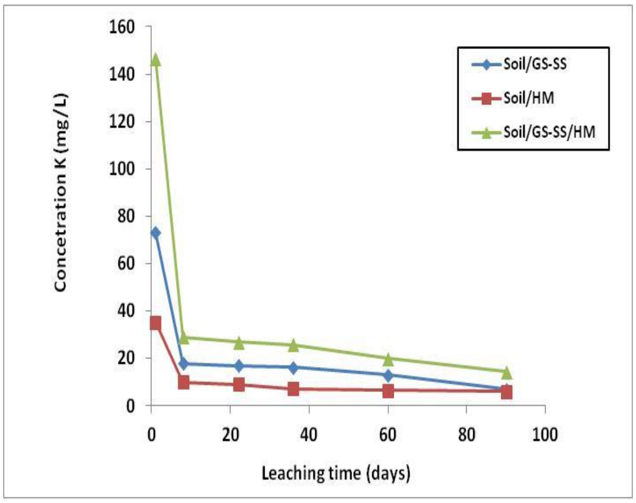


Fig 4. *Concentration of potassium with time*

during field application fungi growing on biochar could capture phosphorous from its surface, allowing its slow uptake by plants. Finally, phenols measured in the leachates were very low, the higher value being obtained from soil/grape skins biochar leaching.

The variation of the chemical oxygen demand values of the leachates with time is shown in Fig. 3. It can be noticed that COD values corresponding to soil/grape skins biochar were higher, while those corresponding to soil/sewage sludge biochar were extremely low to un-measurable. The value corresponding to soil/compost blend was lower than literature data reported for various manure samples [21,22]. When grape skins-sewage sludge biochar was mixed with horse manure, COD was greatly reduced in comparison to grape skins biochar and the drop was remarkable towards the end of the three-month period.

C. *Leaching of Metals from Soil Mixtures*

The cumulative concentrations of major and trace elements in the liquid effluents from all soil mixtures combinations are represented in Table 3. The application of horse manure to the soil increased the extractability of alkali and alkaline earth cations Na, Ca and Mg and this was principally attributed to the soluble forms of carbonates and sulfates in manure incorporating these elements (Table 1). On the other hand, the application of grape skins biochar to the soil resulted in a high release of K in the leachates, associated mainly with the dissolution of arcanite and sylvite minerals present in this material. Upon addition of grape skins-sewage sludge biochar to the soil/manure mixture, it can be observed that the leachability of Na, Ca and Mg cations decreased, revealing that biochar surface provided retention sites for these elements. However, the opposite was true for K, as Fig. 4 also clearly shows.

Concerning heavy metals, Table 3 shows that only Sr and Zn were leached in considerable amounts from all soil mixture combinations, between 223-653 μg/kg and 22-95 μg/kg, respectively. Heavy metals Cu and Mn and environmentally more important toxic metals Cr, Co, Pb and As were not quantified in water extracts. All values were below the European legislation limits [23]. Heavy metal levels from soil/biochar mixtures were about 40-80% lower than those from soil/manure blend, agreeing with earlier studies [2,24]. Nevertheless, these levels were not reduced from application of soil/biochar/manure mixture. The low extractability of above metals could be assigned to the alkaline pH, their possible binding in stable oxides, aluminosilicates or phosphates (such as quartz, hematite, whitlockite magnesian etc., Table 1), or other mechanisms such as competition between elements, complexation, etc. [24,25].

IV. CONCLUSIONS

Grape skins and sewage sludge biochars were richer in Ca, Mg, P, K, Zn and Cu nutrients in comparison to horse manure, which was enriched in Fe and Mn elements.

Application of biochars or manure to a quarzitic soil improved its water holding capacity, increased the pH of water extracts, whereas decreased significantly the electrical conductivity and chemical oxygen demand values with leaching time. For all soil combinations the amount of phenols released in liquid effluents was very low, while that of phosphate ions practically null. By addition of grape skins-sewage sludge biochar to the soil/manure mixture some retention of nitrates, as well as Na, Ca and Mg elements occurred, allowing their slower release from the soil. However, the extractability of K was greatly enhanced, which could be beneficial for K-deficient soils. Heavy metal levels in water leachates were very low and below legislation limits. From soil/biochar mixtutres these were about 40-80% lower than those from soil/manure blend.

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