https://doi.org/10.33263/Materials22.242249

ISSN: 2668-5728 https://materials.international

Materials International

Article

Volume 2, Issue 2, Pages 0242-0249
2020

Received: 01.05.2020
Accepted: 20.05.2020
Published: 25.05.2020

Experimental Study on the Effectiveness of an Untreated Animal Sludge Biochar to Release/Retain Nutrients and Heavy Metals from Soil Amended with Compost

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Abstract: The aim of this work was to examine the suitability of an untreated animal sludge biochar, alone or in combination with municipal solid wastes compost, for amendment of a Mediterranean type soil and reduction of environmental risk. Raw materials were characterized by physical, chemical, and mineralogical analysis, and leaching experiments were carried out simulating field conditions. pH, electrical conductivity, chemical oxygen demand, nitrates, phosphates, phenols, and metals were measured in the leachates. The biochar studied presented greater carbon stability, stronger alkalinity, higher nutrient content, and lower concentration in toxic metals Cr, Pb, and Sr than the compost. Alkali Na and K showed increased solubility, raising the pH of the extracts. Co-application of biochar with compost did not prevent the leaching of nitrogen and phosphorous, reduced the chemical oxygen demand values significantly, allowed the slower release of nutrients to soil and decreased the leachability of heavy metals up to 75%, as compared to soil/compost mixture.

Keywords: animal sludge biochar; municipal solid wastes compost; soil amendment.

1. Introduction

Agricultural production and animal breeding are intensive in most countries around the world, including South European countries, in order to meet global requirements. Hence, to keep soil fertility and avoid environmental problems, appropriate management strategies are mandatory. Composting of organic wastes, for being used as soil ameliorants, is being promoted in the last years. Although the application of such composts improves the physical, chemical, and biological properties of soils, providing organic and inorganic nutrients for plants [1,2], it could also cause eutrophication or contamination of soil and ground waters with toxic metals, if mismanaged [2-4].

The limitations induced by composts have turned scientific attention to the thermal treatment of wastes through pyrolysis, in order to destroy pathogens, generate a carbon-rich product, biochar,

Cite This Article: Vamvuka, D.; Esser, K. Experimental study on the effectiveness of an untreated animal sludge biochar to release/retain nutrients and heavy metals from soil amended with compost. Mat Int **2020**, 2, 0242-0249. https://doi.org/10.33263/Materials22.242249

and simultaneously useful energy from bio-oil and gases produced [4-7]. Biochar has been found to contribute to carbon storage and sequestration and improve soil fertility, to retain nutrients and heavy metals by sorption, adsorption, ion exchange, electrostatic interaction, and other mechanisms [4,6,8]. The properties of biochar depend principally on the raw materials used, as well as on pyrolysis conditions [4-8].

There are many investigations on the effect of biochars on soil quality, using a great variety of biomass materials (woody residues, agricultural straws, sewage sludge), application rates, types of soil, and experimental set up [3,6,9]. As a result, great discrepancies in the performance of biochars were obtained, pointing to the need for separate studies adapted to specific conditions, prior to field applications. Combined treatments of biochars with composts, for more effective utilization of the latter, are limited in the literature. For the production of biochars hardwoods [10], agricultural [1,11], or kitchen wastes and poultry manure [12] have been used, whereas composts originated from mixtures of straw and vegetables [11], wood chips and pig slurry [1], cattle manure [10], or chemical fertilizers [12]. Reported results focused on microbial respiration, fungi/bacteria abundance, uptake of nitrogen, and release of polyaromatic hydrocarbons, Co, Cu and Zn [1,10-12]. To the authors' knowledge, there is a lack of information on the co-application of untreated swine sludge biochar with low-quality compost generated by municipal solid wastes (MSW), the recycling and reuse of which is a hierarchy for European Union (EU) policies on environment and circular economy.

In this context, the current study aimed to examine the suitability of a swine sludge biochar, alone or in combination with MSW compost, for amendment of a Mediterranean type soil and reduction of environmental risk. Raw materials were characterized by physical, chemical, and mineralogical analysis, and leaching experiments were conducted, simulating field conditions. pH, electrical conductivity (EC), chemical oxygen demand (COD), nitrates, phosphates, phenols, and metals were measured in the leachates.

2. Materials and Methods

2.1. Raw materials.

An untreated sludge, from the primary sector of a waste treatment unit of a swine breeding factory (UAS), was used for the production of biochar. The initial moisture content of this sludge was 75%. After air drying, the material was ground in a jaw crusher and a ball mill and sieved to a particle size of < 600 μm. Pyrolysis was conducted in a fixed bed reactor, heated by a temperature-controlled furnace [4]. In a typical test, ~ 20 g of UAS was weighed onto a stainless steel grid holder, placed into the reactor and purged for 30 min with nitrogen (flow rate 100 mL/min). The sample was pyrolyzed at 500°C, at a heating rate of 10°C/min, and retention time 30 min. Volatile products were passed through isopropanol cooled by ice baths. Biochar was collected after cooling the system under nitrogen, weighed, and stored for further tests.

The compost was produced in a local MSW management enterprise. The soil used for the leaching experiments was sampled from the top 20 cm, following the rectangular grid method, at the Chania region in Crete. The < 2 mm fraction was analyzed for its proportions in sand, silt, and clays [13]. Biochar, compost and soil were admixed as follows: biochar/soil 50 g/kg, compost/soil 100 g/kg and biochar/compost/soil 50 g/ 100 g/kg, representing common application rates of 0-100 t/ha [14]. The mixtures were homogenized in glass pots and kept in the dark at about 25°C for one month. During this period, the samples were wetted with de-ionized water and stirred gently periodically.

2.2. Characterization.

Solid materials were characterized by proximate and ultimate analyses, according to European Standards CEN/TC335. Total organic carbon (TOC) was determined by a Carbon analyzer model 572-100 Gasometric. pH and EC were measured with a pH meter Mettler Toledo LE438 and a conductivity meter type EC215 Hanna, respectively, in solid-to-deionized water mixtures of 1:5. For cation exchange capacity (CEC), the ammonium acetate method was employed [15].

Mineral phases were detected by an X-ray diffractometer (XRD), model A8 Advance of Bruker AXS, and identified by DIFFRAC plus Evaluation software and JCPDS database. Chemical analysis in nutrients and heavy metals was performed by an inductively coupled plasma mass spectrometer, model ICP-MS 7500cx of Agilent Technologies, assisted by an Anton Paar Multiwave 3000 oven, for samples digestion.

In the case of liquid extracts through the soil, the pH, EC, and the various elements were determined as mentioned above. A UV-VIS spectrophotometer, type Smart 3 of LaMotte, was used for measuring the COD (by the mercury digestion method 0077-SC), $N\text{-}NO_3$ (by the zinc reduction method 3689-SC), $P\text{-}PO_4$ (by the vanadomolybdophosphoric acid method 3655-SC) and phenols (by the aminoantipyrine method 3652-SC).

2.3. Leaching through the soil.

PVC columns with ID=4.5 cm and H=50 cm, fitted with fiberglass into the drain opening and a valve at the base, were used for the leaching tests. About 100 g of each mixture was packed into the column and saturated with de-ionized water. Keeping the hydraulic head constant on the basis of communicating vessels, leaching started by percolating de-ionized water through the column and collecting the effluents at different time intervals. In order to simulate rainfall conditions in the region of Chania, Crete, leaching was discontinuous, lasted three months, and the amount of water corresponded to the average annual quantity of rainfall in the area (~600 mm). Two replicates were carried out for each solid mixture, and measured parameters were averaged (error ± 3%). Leachates were filtered through micropore membrane filters before analyses.

3. Results and Discussion

3.1. Characterization of soil, compost and biochar.

Comparing compost and UAS biochar in Table 1, it can be observed that the amount of ash and organic matter were similar, whereas the fixed carbon content of biochar was higher, implying greater stability when applied to soil [5]. Additionally, the higher carbon stability and aromaticity of UAS biochar are reflected by its lower H/C and O/C molar ratios with respect to compost, which is important for carbon sequestration in soils [4,5]. On the other hand, although the nitrogen content of biochar was quite high due to the protein content of the raw material (animal sludge), the N/C was lower than that of compost and, consequently it's potential to release nutrient nitrogen for plants.

The high pH and very small EC values of the soil and UAS biochar, as shown in Table 1, are expected to have a positive effect on soil amelioration and the leachability of nutrients or toxic metals from soil system, however, the increased amount of soluble salts in compost, as measured by the EC, could have an opposite effect, tending to decrease nutrients and water uptake by plants, when applied to soils [3]. Nevertheless, the compost presented the highest CEC value among the solids studied, revealing an increased capacity for adsorbing cation nutrients, which are essential for plants [5]. The soil had a low CEC, due to its quarzitic nature (sand 53%, silt 43%, clays 4%).

The mineral phases of the samples, identified by XRD analysis, are illustrated in Figure 1. The soil consisted principally of quartz and of smaller amounts of muscovite and rutile.

Table 1. Physicochemical properties, proximate, and ultimate analyses of solids (% dry).

Sample	Soil	Compost	Biochar
pH	8.2	7.7	9.0
EC (mS/cm)	0.05	6.5	0.84
CEC (meq/100g)	4.0	65.4	24.8
Volatiles	1.3	22.7	13.1
Fixed carbon	0.9	26.9	37.8
Ash	97.8	50.4	49.1
C	0.25	24.7	33.8
H	0.16	2.6	1.5
N	0.04	3.0	2.8
O	1.7	13.7	11.7
S	-	0.38	1.1
TOC	0.01	4.2	31.3
H/C	7.6	1.26	0.53
O/C	5.4	0.41	0.26
N/C	0.15	0.10	0.07

The compost was dominated by calcite and quartz. It also contained some clays, i.e., microcline, muscovite, and albite. Phosphorus was incorporated in hydroxyapatite, while the potassium in sylvite and aphthitalite. UAS biochar was enriched in Ca, Mg, P, and Fe minerals in the forms of calcite, anhydrite, whitlockite magnesian, and rodolicoite. A considerable amount of quartz and smaller of hematite was also detected. Potassium was bound in fairchildite.

The concentrations of major elements in compost and biochar are compared in Figure 2a. As can be noticed, UAS biochar presented a greater nutrient content in Ca, Mg, P, but also in Fe and K than the compost under study. The high percentage of Ca and P is typical of animal wastes [16,17]. The level of these elements is similar or higher than other biochar materials reported in the literature [5,6,9,10], implying that present biochar could be used for soil amendment. However, the solubility of the minerals incorporating these elements governs the bioavailability of nutrients in soils [9].

As concerns trace elements, Figure 2b shows that UAS biochar contained elevated amounts of micronutrients Mn, Cu and Zn (Zn in biochar was 3710 mg/kg, in compost 257 mg/kg; not plotted due to difference in scale) and much lower concentrations in toxic heavy metals Cr, Pb and Sr, as compared to compost. The level of As of these materials was comparable. Hazardous species Hg, Cd, and Co were below detection limits. Measured trace element values were within limits set by EU directives for disposal in landfills [18].

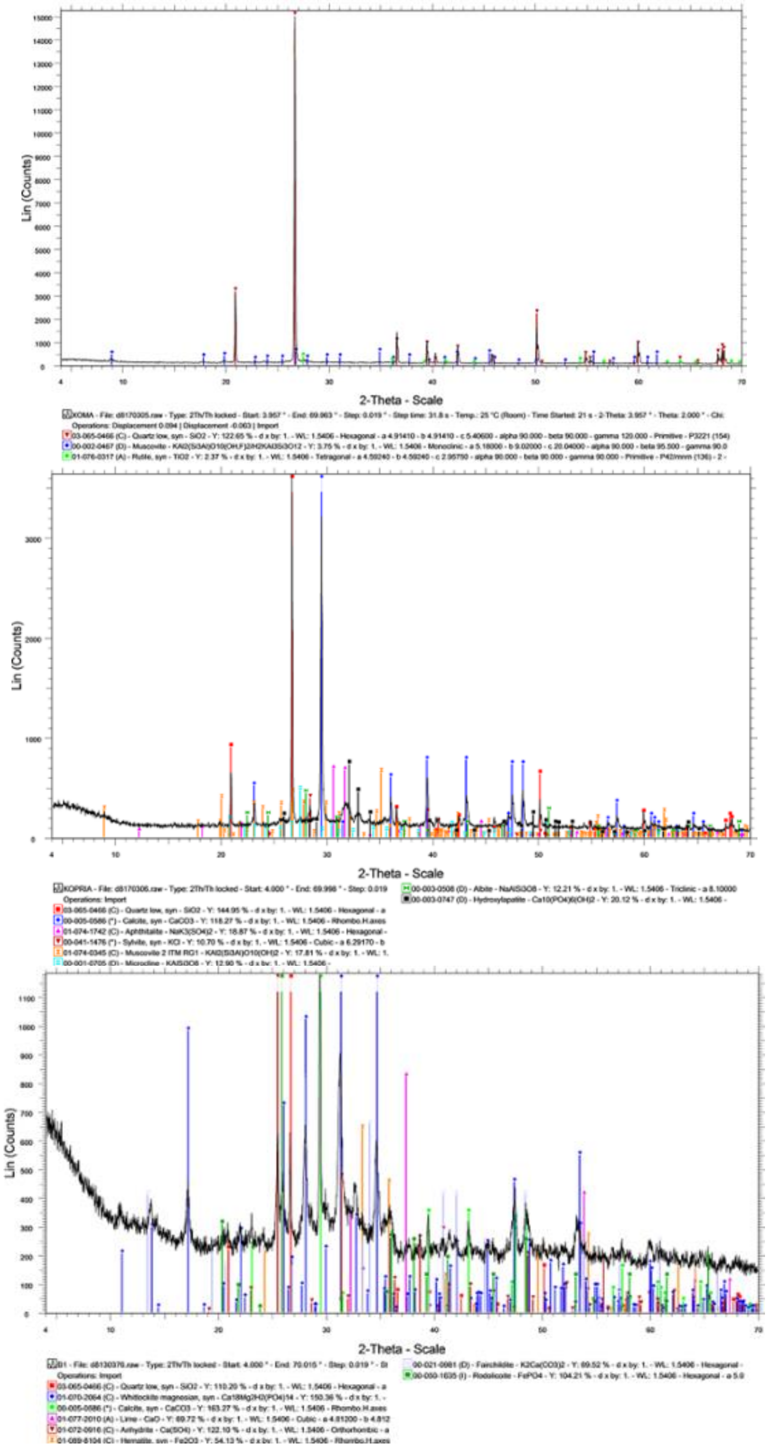

Figure 1. XRD spectra of soil, compost, and UAS biochar.

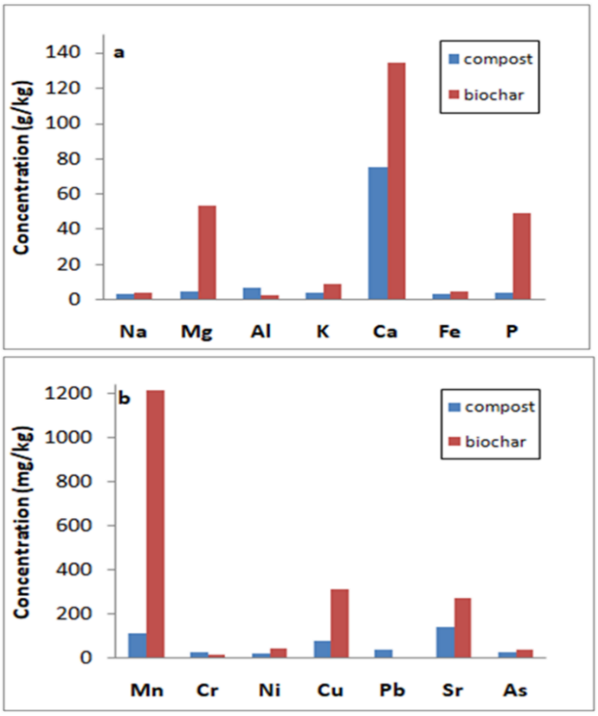

Figure 2. Chemical analysis of compost and biochar in (a) major and (b) trace elements.

3.2. Leaching behavior of ions and species from soil/compost/biochar mixtures.

In Table 2, the variation of pH, EC, nitrate, and phosphate ions, as well as of phenols with leaching time is represented. pH values were similar for leaching of compost, biochar, or their mixture through the soil and increased gradually with time from 7.7 to 8.6. This increase was attributed to the potential dissolution of Ca and K based alkaline substances in water extracts, during the tests. On the other hand, EC was extremely low, especially upon leaching of biochar and dropped to nearly zero values after the release of soluble salts at the beginning of the experiment.

As clearly seen in Table 2, practically no nitrates were leached from UAS biochar, in contrast to compost. Although the nitrogen content of biochar was nearly the same as that of compost, it could probably be bound in heterocyclic nitrogen compounds not easily solubilized [19]. When the biochar was added to the soil/compost mixture, nitrification of effluents was not inhibited, implying that nitrates could not be adsorbed on biochar surface. In a previous work by the authors, this behavior has been explained by the negative surface charge of biochar [20]. According to some studies [21], the effect could be positive in terms of efficient use of compost nitrogen for plant nutrition.

Regarding the concentration of phosphates in the water extracts, it can be noticed that less phosphorous was measured in the first leachate of compost/biochar mixture through the soil, as compared to compost, and this tended to decrease with time. The extractability of phosphate ions is associated with the mineral phases in which phosphorous is incorporated. As previously shown by the XRD analysis, UAS biochar contained insoluble whitlockite magnesian and rodolicoite. However, the considerable amount leached could be assigned to the negative charge of the biochar surface at the alkaline pH of the tests, which could adsorb cations of Ca, Mg or Fe of phosphates, leading to their precipitation in liquid effluents [4,6,22]. Finally, phenols leached from all solid materials were very low.

Changes of COD, as a function of leaching time, are illustrated in Figure 3. As can be seen, the COD corresponding to compost was significantly higher than that of biochar and also higher than literature data for composts produced by different wastes [23,24]. Admixing the biochar to the soil/compost system resulted in a great reduction of the COD values. This could be assigned to the adsorption of organic and inorganic species from soil and water on the O-rich biochar surface [24].

3.3. Leaching behavior of metals from soil/compost/biochar mixtures.

Table 3 compares the cumulative concentrations of major and trace elements in the leachates. Among major elements, Na and K were extracted in higher amounts from all soil combinations.

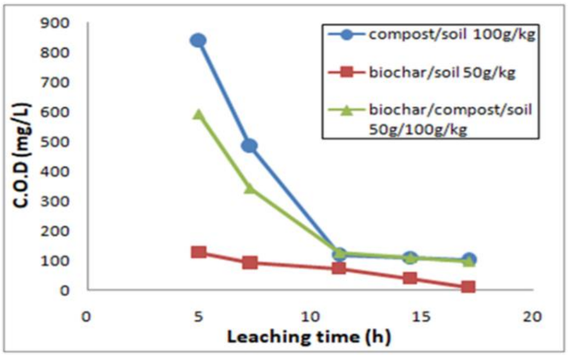

Figure 3. Variation of leachates COD with time.

The increased migration of Na through soil is related to its great affinity with water. The leachability of K was correlated to the solubility of sylvite and fairchildite present in compost and biochar, respectively. The lower extractability of Ca and Mg were attributed to the incorporation of these elements to a high extent in phosphates. When UAS biochar was added to soil or soil/compost mixture, as can be observed, the mobility of major elements was reduced between 23% and 80%, suggesting that biochar provided retention sites for nutrient elements.

In relation to heavy metals, Table 3 shows that those who were released in higher quantities in liquid effluents were Cu, Zn, and Sr, reaching levels between 300 μg/kg and 972 μg/kg. Cu presented the highest mobility. The concentrations of Hg and Cd in the extracts were below detection limits. Upon addition of UAS biochar to soil metals Mn, Co, Ni, Cu, Zn, and Pb were not leached at all, whereas Cr, As, and Sr was measured in minor amounts, reduced by 65-96%, in comparison to soil/compost mixture.

Table 2. Variation of pH, EC, ions and phenols in the leachates as a function of time.

	Leaching time (h)		
	5	11.3	17.1
Compost/soil			
pH	7.7	7.9	8.6
EC (mS/cm)	2.6	0.3	0.3
NO_3^-(mg/L)	230	-	-
PO_4^{3-}(mg/L)	292	95	11
Phenols (mg/L)	8.0	4.6	3.5
Biochar/soil			
pH	7.8	8.0	8.0
EC (mS/cm)	0.7	0.4	0.4
NO_3^-(mg/L)	3.0	-	-
PO_4^{3-}(mg/L)	318	148	105
Phenols (mg/L)	2.40	0.56	0.44
Biochar/compost/soil			
pH	8.0	8.3	8.4
EC (mS/cm)	2.5	0.7	0.6
NO_3^-(mg/L)	330	-	-
PO_4^{3-}(mg/L)	209	157	98
Phenols (mg/L)	0.92	0.56	0.40

Table 3. Cumulative concentrations of major and trace element in leachates, relative mass leached (%).

	Major element concentration (mg/kg)					
	Na	Mg	Al	K	Ca	Fe
Soil	40.3 (22.4)	1.9 (0.2)	-	6.8 (7.5)	15.1 (1.7)	-
Compost/soil	583.4 (37.1)	56.9 (3.5)	69.6 (0.9)	378.8 (16.3)	144.8 (0.5)	30.1 (0.8)
Biochar/soil	120.3 (13.2)	248.8 (4.6)	1.0 (-)	163.7 (9.1)	18.2 (0.1)	0.8 (-)
Biochar/compost/soil	547.1 (27.4)	192.3 (2.7)	50.8 (0.6)	533.6 (16.8)	78.4 (0.2)	21.2 (0.5)

	Trace element concentration (μg/kg)							
	Cr	Ni	Mn	Cu	Zn	As	Pb	Sr
Soil	-		0.45 (0.01)	-	-	-	-	111.3 (1.3)
Compost/soil	94.9 (0.7)	62.7 (0.9)	122.4 (0.2)	459.9 (1.6)	439.4 (0.4)	29.6 (0.3)	22.6 (0.1)	580.2 (0.7)
Biochar/soil	3.9 (0.1)	2.0 (-)	53.8 (-)	-	35.3 (-)	10.5 (0.3)	-	48.6 (0.1)
Biochar/compost/soil	37.9 (0.2)	48.1 (0.4)	123.3 (0.1)	972.0 (1.6)	423.0 (0.1)	89.7 (0.7)	20.7 (0.1)	300.6 (0.3)

Furthermore, when a combination of soil/compost/biochar was used, the concentrations of all heavy metals (apart from Cu and As) and their mobility were decreased significantly up to 60% and 75%, respectively, as compared to soil/compost blend. Legislation limits stipulated by EU directives for soil leachates were kept in all cases [25].

The leachability behavior of the various species studied is complex and influenced by numerous factors, such as the mineralogical and chemical compositions of the solids and their physicochemical properties, mainly CEC and pH. Obviously, the low mobility of elements through the soil was attributed to a high degree to the alkaline pH of the soil system [1,3,4,6,21]. Taking into consideration the low CEC of the soil, the UAS biochar was responsible for the retention of metals. The mechanisms proposed include sorption, electrostatic attraction, competition between elements, precipitation, or complexation [26]. The low extractability of Mn, Co, Ni, Cu, Zn, Pb, Cr, and Sr implies that they could be bound in stable oxide surfaces or phosphates identified in biochar, such as quartz, hematite, lime, and whitlockite magnesian and rodolicoite, respectively. On the other hand, the increased mobility of As when compost and biochar were applied to the soil, could be ascribed to its negative oxidation state under the alkaline conditions of the experiments, which did not favor its retention by the above mechanisms.

4. Conclusions

The UAS biochar presented greater carbon stability and stronger alkalinity than the compost studied. Also, it had higher nutrient and micronutrient content in Ca, Mg, P, Fe, K, Mn, Cu, and Zn, while the lower concentration in toxic heavy metals Cr, Pb, and Sr. The application of biochar to soil/compost mixtures did not prevent the leaching of nitrates or phosphates in water extracts, however, reduced the COD values significantly. For all soil/compost/biochar blends, the elements which were released in higher amounts were Cu, Zn, and Sr among trace and alkali Na and K among major elements, which increased the pH of liquid effluents. The concentrations of heavy metals leached from UAS biochar were very low, and upon its addition to soil/compost mixture, they were significantly reduced, up to 60%, as compared to soil/compost blend and were well below legislation limits for soil leachates. Therefore, the co-application of biochar with compost could be beneficial for the soil amendment, allowing the slower release of nutrients to soil and retention of toxic heavy metals.

Funding

This research received no external funding.

Acknowledgments

The authors kindly thank the laboratories of Hydrogeochemical Engineering and Soil Remediation, Management of mining/metallurgical wastes and Applied Mineralogy of the Technical University of Crete, for the ICP-MS, UV-VIS, and XRD analyses.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Liang, J.; Yang, Z.; Tang, L.; Zeng, G.; Yu, M.; Li, X.; Wu, H.; Qian, Y.; Li, X.; Luo, Y. Changes in heavy metal mobility and availability from contaminated wetland soil remediated with combined biochar-compost. *Chemosphere* **2017**, *181*, 281-288, https://doi.org/10.1016/j.chemosphere.2017.04.081.
2. Cambier, P.; Michaud, A.; Paradelo, R.; Germain, M.; Mercier, V.; Guérin-Lebourg, A.; Revallier, A.; Houot, S. Trace metal availability in soil horizons amended with various urban waste composts during 17 years – Monitoring and modelling. *Science of The Total Environment* **2019**, *651*, 2961-2974, https://doi.org/10.1016/j.scitotenv.2018.10.013.
3. Gondek, K.; Mierzwa-Hersztek, M.; Kopec, M. Mobility of heavy metals in sandy soil after application of composts produced from maize straw, sewage sludge and biochar. *J. Environ. Manag.* **2018**, *210,* 87–95, https://doi.org/10.1016/j.jenvman.2018.05.035.
4. Vamvuka, D.; Sfakiotakis, S.; Pantelaki, O. Evaluation of gaseous and solid products from the pyrolysis of waste biomass blends for energetic and environmental applications. *Fuel* **2019**, *236,* 574–582, https://doi.org/10.1016/j.fuel.2018.08.145.
5. Cely, P.; Gasco, G.; Paz-Ferreiro, J.; Mendez, A. Agronomic properties of biochars from different manure wastes. *J. Anal. Appl. Pyrolysis* **2015**, *111*, 173–182, https://doi.org/10.1016/j.jaap.2014.11.014.
6. Manolikaki, I.I.; Mangolis, A.; Diamadopoulos, E. The impact of biochars prepared from agricultural residues on phosphorus release and availability in two fertile soils. *Journal of Environmental*

Management **2016**, *181*, 536-543, https://doi.org/10.1016/j.jenvman.2016.07.012.
7. Vamvuka, D.; Sfakiotakis, S. Thermal Behaviour and Reactivity of Swine Sludge and Olive By-Products During Co-pyrolysis and Co-combustion. *Waste and Biomass Valorization* **2019**, *10*, 1433-1442, https://doi.org/10.1007/s12649-017-0118-4.
8. Sfakiotakis, S.; Vamvuka, D. Thermal decomposition behavior, characterization and evaluation of pyrolysis products of agricultural wastes. *Journal of the Energy Institute* **2018**, *91*, 951-961, https://doi.org/10.1016/j.joei.2017.09.001.
9. Limwikran, T.; Kheoruenromne, I.; Suddhiprakarn, A.; Prakongkep, N.; Gilkes, R.J. Dissolution of K, Ca, and P from biochar grains in tropical soils. *Geoderma* **2018**, *312*, 139-150, https://doi.org/10.1016/j.geoderma.2017.10.022.
10. 1. Ippolito, J.A.; Stromberger, M.E.; Lentz, R.D.; Dungan, R.S. Hardwood biochar and manure co-application to a calcareous soil. *Chemosphere* **2016**, *142*, 84-91, https://doi.org/10.1016/j.chemosphere.2015.05.039.
11. Ye, S.; Zeng, G.; Wu, H.; Liang, J.; Zhang, C.; Dai, J.; Xiong, W.; Song, B.; Wu, S.; Yu, J. The effects of activated biochar addition on remediation efficiency of co-composting with contaminated wetland soil. *Resources, Conservation and Recycling* **2019**, *140*, 278-285, https://doi.org/10.1016/j.resconrec.2018.10.004.
12. Sadaf, J.; Shah, G.A.; Shahzad, K.; Ali, N.; Shahid, M.; Ali, S.; Hussain, R.A.; Ahmed, Z.I.; Traore, B.; Ismail, I.M.I.; Rashid, M.I. Improvements in wheat productivity and soil quality can accomplish by co-application of biochars and chemical fertilizers. *Science of The Total Environment* **2017**, *607-608*, 715-724, https://doi.org/10.1016/j.scitotenv.2017.06.178.
13. Bouyoucos, G.J. A Recalibration of the Hydrometer Method for Making Mechanical Analysis of Soils1. *Agronomy Journal* **1951**, *43*, 434-438, https://doi.org/10.2134/agronj1951.00021962004300090005x.
14. Jeffery, S.; Verheijen, F.G.A.; van der Velde, M.; Bastos, A.C. A quantitative review of the effects of biochar application to soils on crop productivity using meta-analysis. *Agriculture, Ecosystems & Environment* **2011**, *144*, 175-187, https://doi.org/10.1016/j.agee.2011.08.015.
15. Sumner, M.E.; Miller, W.P. Cation exchange capacity and exchange coefficients. In: *Methods of Soil Analysis Part 3. Chemical Methods*. Bingham, J.M. Ed.; ASA-SSSA Madison: Wisconsin, WI, USA, 1996; pp. 1201–1229, https://doi.org/10.2136/sssabookser5.3.c40.
16. Huang, Y.; Dong, H.; Shang, B.; Xin, H.; Zhu, Z. Characterization of animal manure and cornstalk ashes as affected by incineration temperature. *Applied Energy* **2011**, *88*, 947-952, https://doi.org/10.1016/j.apenergy.2010.08.011.
17. Vamvuka, D.; Dermitzakis, S.; Pentari, D.; Sfakiotakis, S. Valorization of Meat and Bone Meal through pyrolysis for soil amendment or lead adsorption from wastewaters. *Food and Bioproducts Processing* **2018**, *109*, 148-157, https://doi.org/10.1016/j.fbp.2018.04.002.
18. Point 6 of the draft agenda FWG 2 June 2014: Revision of the Fertilisers Regulation: (a) Feedback of the FWG members on essential safety requirements discussed on 17 March 2014; Spain, 2014. Available online: https://ec.europa.eu/transparency/regexpert/index.cfm?do=groupDetail.groupDetailDoc&id=13108&no=5 accessed on 13 March 2020.
19. Knicker, H. "Black nitrogen" – an important fraction in determining the recalcitrance of charcoal. *Organic Geochemistry* **2010**, *41*, 947-950, https://doi.org/10.1016/j.orggeochem.2010.04.007.
20. Alexandrakis, S. Environmental pollution of soils from deposition of ashes produced by co-combustion of urban and agricultural wastes of Chania region in Crete. MSc Thesis, Technical University of Crete, 2019.
21. Yuan, H.; Lu, T.; Wang, Y.; Chen, Y.; Lei, T. Sewage sludge biochar: Nutrient composition and its effect on the leaching of soil nutrients. *Geoderma* **2016**, *267*, 17-23, https://doi.org/10.1016/j.geoderma.2015.12.020.
22. Iqbal, H.; Garcia-Perez, M.; Flury, M. Effect of biochar on leaching of organic carbon, nitrogen, and phosphorus from compost in bioretention systems. *Science of The Total Environment* **2015**, *521-522*, 37-45, https://doi.org/10.1016/j.scitotenv.2015.03.060.
23. Lu, K.; Yang, X.; Gielen, G.; Bolan, N.; Ok, Y.S.; Niazi, N.K.; Xu, S.; Yuan, G.; Chen, X.; Zhang, X.; Liu, D.; Song, Z.; Liu, X.; Wang, H. Effect of bamboo and rice straw biochars on the mobility and redistribution of heavy metals (Cd, Cu, Pb and Zn) in contaminated soil. *Journal of Environmental Management* **2017**, *186*, 285-292, https://doi.org/10.1016/j.jenvman.2016.05.068.
24. Yang, X.Y.; Chang, K.H.; Kim, Y.J.; Zhang, J.; Yoo, G. Effects of different biochar amendments on carbon loss and leachate characterization from an agricultural soil. *Chemosphere* **2019**, *226*, 625-635, https://doi.org/10.1016/j.chemosphere.2019.03.085.
25. EBC. European Biochar Certificate, Guidelines for a Sustainable Production of Biochar, Version 4.8. European Biochar Foundation (EBC), Arbaz, Switzerland. Available online: http://www.european-biochar.org/en/download accessed on 7 July 2014.
26. Boostani, H.R.; Najafi-Ghiri, M.; Hardie, A.G.; Khalili, D. Comparison of Pb stabilization in a contaminated calcareous soil by application of vermicompost and sheep manure and their biochars produced at two temperatures. *Applied Geochemistry* **2019**, *102*, 121-128, https://doi.org/10.1016/j.apgeochem.2019.01.013.