Extra CO₂ sequestration following reutilization of biomass ash

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Abstract

Although combustion ashes are usually used in soils, little attention is paid to the CO₂ sequestration potential of this practice. The present study aims to quantify carbon sequestration as carbonate compounds in a tailored synthetic calcareous soil treated with biomass ash from a gasification power plant that uses olive cake. It is estimated that after ash amendment, 14.5 g CO₂ remained fixed per kg of fly biomass ash, 16.5 g CO₂ per kg of bottom biomass ash with plant cultivation and 19.7 g CO₂ per kg of bottom biomass ash without plant cultivation. This inorganic C fixation plus the organic (black) C contained in the ashes made the reutilization of ashes as K fertilizer a relevant practice due to its C resilience and rate, with a yearly C sequestering potential of ca. 8% of 'Soil carbon 4 per mille' goal, an initiative launched at the COP21.

Keywords: Potassium; fertilizer; black carbon; olive cake; soil carbonates

Abbreviations: BA, biomass ash; FBA, fly biomass ash; BBA, biomass bottom ash; TGA, thermo-gravimetric analysis; DTG, differential thermogravimetry; BECCS, bioenergy with carbon capture and storage; TSC, theoretical CO₂ sequestration capacity.

1. Introduction

Biomass represents 8-15% of the world energy supplies as electricity, heat and fuels for transportation and would contribute up to 33–50% of the world's current primary energy consumption by 2050. The demand for bioenergy is increasing worldwide. In addition to wood fuels (Huotari et al., 2015), diverse biomass varieties with distinct source and origin can be used as solid biofuel resources (Vassilev et al., 2013c). Among them, the agro-industry offers many biomass wastes (shells, pits, fruits, seeds, coir, bagasse, fodder, pulps, cakes) from various species, with adequate characteristics to be used as biofuels, and that are produced in vast amounts in the processing plants. Among agro-industry wastes, large amounts of residues from the olive oil industry are produced every year in the Mediterranean areas (Barbanera et al., 2016; Buratti et al., 2016). Particularly in Andalusia, Southern Spain, 1.2×10^6 Mg year⁻¹ of dry olive cake are produced. Due to its adequate higher calorific value (4200 kcal kg⁻¹) this olive industry waste is being extensively used for energy production, both for heat (24% of the yearly production) and electricity generation (45% of the yearly production) (data for 2015, Agencia Andaluza de la Energía, 2016). Additional information about other olive wastes and uses can be found elsewhere Manzanares et al., (2017).

Biomass ash (BA) is the solid residue that results from the direct combustion of biomass. Some 476 million Mg of BA are generated yearly assuming 6.8% mean ash yield on biomass dry basis (Vassilev et al., 2013a). This BA is a complex inorganic–organic mixture with a variable composition depending on the feedstock and combustion. The ash is generated as a combustion by-product, whether for heat or power generation, but it has

potential use as a fertilizer in forests (Pitman, 2006). Recycling of wood ash as forest fertilizer has been practiced for a long period of time with this tradition having its main focus in boreal forests (Fernández-Delgado Juárez et al., 2015). Use of BA has several known environmental advantages e.g., favours the recycling of nutrients, avoids acidification, improves tree yield and reduces waste dumps (Huotari et al., 2015). Although the use of BA for soil improvement and fertilization has been studied extensively (Cruz-Paredes et al., 2017; Vassilev et al., 2013b), most of the studies dealt with wood ash use in forest systems (Demeyer et al., 2001).

Agricultural biomass tends to be richer in fertilizer elements, such as K and P, than wood biomass (Vassilev et al., 2013a). BA from straw, shells, olive residues, miscanthus, rice husk, etc., can be used to fertilize agricultural soils at low dose rates which maximizes benefits while avoiding toxicity effects found in forest systems when BA applications are in excess of 10 Mg ha⁻¹ (Pitman, 2006). Despite the potential value of BA, the ash is regarded as a waste product according to European legislation and many countries lack regulations or recommendations concerning ash fertilization (Huotari et al., 2015).

It is widely accepted that biomass is a renewable energy resource that does not contribute to the greenhouse effect due to the CO₂-neutral conversion. Particularly, the biomass from agro-industrial factories is highly enriched in alkaline and alkaline-earth constituents which can contribute significantly to the capture of CO₂ by forming carbonates as a result of solid-gas reaction between the CO₂ released during biomass burning or atmospheric, and Ca, K, Mg and Na oxy-hydroxides that are formed during biomass combustion (Vassilev et al., 2013a).

If the CO₂ in the carbonates is fixed and immobilized, some extra carbon capture and storage is added. However, ultimately, the factor responsible for ash stability is calcite solubility. In acid soils, ash can be used as a liming agent (Zhang et al., 2001; Zhang et al., 2002). In these soils, the ash particles will be continuously re-dissolved, most of the Ca²⁺ will leach and the original soil pH will be recovered.

On the contrary, if BA is applied to calcareous soils it could be hypothesized that the carbonate compounds which originated from the BA would be stable, leading to a permanent CO₂ immobilization and a true extra carbon capture. Calcareous soils are distributed worldwide, occupying over 600 x 10⁶ ha worldwide (Leytem and Mikkelsen, 2005). Despite the fact that BA and other types of ash have usually been added to soils, mainly agronomical or forestry effects have been considered and little attention has been paid to the potential of this practice for CO₂ sequestration. In a review dealing with coal combustion fly ash, Ukwattage et al. (2013) acknowledged that fly ash addition to soils can catalyse both organic carbon sequestration reactions and the mineral sequestration but also indicated that no research in the literature has revealed the overall contribution of fly ash in soil sequestration since it seems challenging to quantify.

The present study aims to determine how much carbon is captured in the form of carbonate compounds in a model synthetic calcareous soil treated with biomass ash coming from oil cake used in electricity generation.

Knowledge of this extra carbon-capturing capacity of ashes will help to complete the life cycles of solid wood products. At present, the sustainable

implementation of this approach is rather insufficient due to a lack of sufficient basic knowledge (Matthews et al., 2014; Vassilev et al., 2013b).

2. Materials and methods

2.1. Ashes

Biomass bottom ash (BBA) and fly biomass ash (FBA) were used in this study. The BBA comes from the broiler itself and it was immediately moistened after extraction, while FBA was obtained from the flue gas discharge system by mean of an electrostatic air filter. The ashes were taken in a biomass generation plant in Fuente de Piedra, Málaga, Spain (Neoelectra S.A). This power plant (7.8 MW) mainly uses olive cake (dry solid residue obtained after olive oil chemical extraction known as 'orujillo' in Spanish), although it is mixed with shredded hybrid poplar and pine chips in lesser amounts (<50% both). The production of ashes was 2.5 % w/w of the biomass feed.

2.2. Incubation experiment

An incubation experiment in which BBA and FBA were mixed with a synthetic calcareous soil was carried out in order to study the carbonation process of ashes. Due to the low ash ratio required, the differentiation of the newly-formed carbonated species from the species already present in the soil would be a challenging task. To overcome this, a synthetic model soil was

prepared in which carbonate compounds of different origins could be separated by sieving.

The synthetic soil components included (1) silica sand (87.8 %) (Axton-Leroy Merlin, Alcobendas, Madrid, Spain), as the major component of the soil, with particle size 0.5-2 mm and pH 6.02; (2) limestone (9.8%) (Santo Angel Mining Co., Gilena, Sevilla, Spain), with particle size 2-4 mm; (3) white peat (1.9%) (Naturplant SA, Los Palacios, Sevilla, Spain) with particle size 63 µm-0.5 mm as organic component of soil (4); pruning waste compost (0.1 %) (Naturplant SA, Los Palacios, Sevilla, Spain) with particle size 63 µm-0.5 mm as source of microorganisms; (5) and the added BBA or FBA (0.50 %) with particle size 63 µm-0.5 mm. Before use, all the components except the pruning waste compost were oven-dried (70°C), ground and sieved to obtain the chosen particle size. Limestone was wet sieved to wash fine particles (<2 mm) through.

Mixtures were prepared by mixing the components needed to fill one 200 cm³ pot, that was 358.8 g (ash included). A finely meshed nylon cloth was placed at the bottom of the pot to avoid loss of fine particulate material. All the pots were watered during 25 days and then sown with sunflower seeds (*Helianthus annuus* var P63 LL104, Pioneer Hi-Bred Spain, S.L., Sevilla, Spain). The treatments were named as BBAs-pl and FBAs-pl. Additional pots were prepared in the same way but not planted, as control treatments (BBAs-no and FBAs-no) to assess the effect of plant (root) on carbonation. Four pots per treatment were prepared and randomly distributed in the greenhouse.

Pots were regularly watered (3 times per week) with enough distilled water (50 cm³ per pot) to obtain a small volume of leachate that was retained in a dish that was placed below the pot. Commercial liquid fertilizer (25 mL per pot of a

solution containing 500 mg N L⁻¹, 500 mg P₂O₅ L⁻¹, 500 mg K₂O L⁻¹, 2.5 mg Fe L⁻¹, 1.7 mg Cu L⁻¹, 1.7 mg Mn L⁻¹, 0.8 mg Zn L⁻¹) was supplied once every 2 weeks. Sunflower plants were cut off 84 days after sowing and fresh and dry aerial biomass of each plant was weighed.

At the end of the experiment, the soil of each pot was dried at 70°C, weighed, and sieved with 2 mm and 0.5 mm sieves. This temperature (70°C) was selected to avoid dust produced in sieving operations when drying at higher temperatures. Results were corrected by residual moisture at 70 °C. The recovery for each particle size (> 2 mm, 0.5-2 mm and <0.5 mm) was expressed as a percentage in relation to the weights of the soil components that were initially included in each fraction. The fraction <0.5 mm of each pot was ground to a fine powder in an agate mortar aided with liquid nitrogen and homogenized before isotopic and TGA analyses.

2.3. Analytical determinations

Electrical Conductivity (E.C.) and pH were determined with electrodes placed in a soil–water 1:2.5 solution or, in the case of ashes, a 1:5 ash–water ratio. Total carbonate was determined by the pressure-calimeter method (Ministerio_de Agricultura, 1986) and expressed as CaCO₃.

Aqua regia extracts for metal analysis obtained by microwave-assisted digestion of the feedstock samples were used for mineral nutrients and trace elements which were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) (Dahlquist and Knoll, 1978).

Theoretical CO₂ sequestration capacity (TSC) has been calculated using the Stenoir stoichiometric formula (Eq. 1), based on the reaction of alkaline oxides in the waste to form carbonates (Tamilselvi Dananjayan et al., 2016):

$$\begin{aligned} \text{(Eq. 4)} \quad \text{CO}_2 (\%) &= 0.785 (\% \text{CaO} - 0.7 \% \text{SO}_3) + 1.09 \% \text{MgO} \\ &+ 0.71 \% \text{Na}_2\text{O} + 0.468 \% \text{K}_2\text{O} \end{aligned}$$

Elemental and isotopic measurements were carried out in the feedstock soil components and in the particle size fraction <0.5 mm at the end of the incubation experiment. Natural ¹³C abundance has been widely used as an organic contribution tracer as well as for studies of the soil organic matter dynamics. The <0.5 mm used fraction is likely to include the organic matter and the ash. Four replicated samples were analyzed. The stable carbon isotopic signature (δ¹³C) was analyzed using a Flash 2000 HT/IRMS system (Thermo Scientific, Bremen, Germany). The micro-analyzer was coupled via a ConFlo IV interface unit to a continuous flow Delta V Advantage isotope ratio mass spectrometer (IRMS) (Thermo Scientific, Bremen, Germany). The combustion furnace was set at 1020 °C and the sample size was ca.1.00 mg wrapped in tin foil. Isotopic ratios are reported as parts per thousand (‰) deviations (expressed as δ values) referred to the appropriate standard (Vienna Pee Dee Belemnite; VPBD), as recognized by the International Atomic Energy Agency (IAEA) (Valkiers et al., 2007) following Eq. 1:

$$\delta = [(R \text{ sample} - R \text{ standard}) / (R \text{ standard})] \times 1000 \quad \text{Eq.1}$$

where R is the ¹³C/¹²C ratio.

The standard deviations of δ¹³C were typically less than ± 0.05 ‰.

In the same samples, thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) were conducted using a thermo-gravimetric analyzer (Mettler Toledo TGA/DSC1 STARe System). These experiments were performed by heating a 50-130 mg sample from 25 °C to 900 °C under oxidizing conditions as the flow rate of air was 20 ml min⁻¹ and the heating rate was at 5 °C min⁻¹. The 4 replicated soil samples corresponding to each treatment were separately analyzed and the average values for TGA and DTG of the four samples were plotted. TGA measures the mass variation of a sample when it is subjected to heating. This procedure allows obtaining knowledge of combustion properties of carbonaceous materials and combined with DTG it serves to obtain information about ash composition (Fernández et al., 2012).

For the statistical analysis, comparisons of treatments were made by using the Tukey HSD test or using the independent-samples t-test when appropriate. Calculations were carried out by using SPSS v.22.

3. Results and discussion

3.1. Ashes

The composition of ashes is shown in Table 1. Contents of major cations in FBA followed the order K₂O>CaO>MgO>>Na₂O and in BBA followed the order CaO>K₂O>MgO>>Na₂O. Increased concentration of K compounds in FBA compared to BBA was probably caused by volatilization of K compounds in the broiler. The average K content for both ashes (234 g K₂O kg⁻¹) was similar to that previously reported (250 g K₂O kg⁻¹) by Fernández-Llorente and Carrasco-

García (2005 for 'orujillo' ash obtained in the laboratory. The high K and P contents in both ashes support their use as K fertilizer. Only a few countries in Europe have regulations or recommendations concerning ash fertilization. Finnish legislation establishes that ash used as a forest fertiliser must have a combined concentration of P and K exceeding 2%, and at least 6% of Ca (Huotari and Metla, 2012). Such specifications are fully met by both ashes from olive residues. Contents of As, Pb and Zn were higher in FBA than in BBA (ca. 3 to 6 times). However, the trace metal contents in both ashes could be considered as low to moderate. Finnish legislation specifies that the maximum concentrations allowed for cadmium in ash may not exceed 25 mg kg^{-1} , and the arsenic concentration must not exceed 40 mg kg^{-1} (Huotari and Metla, 2012). The Cd contents of the studied olive cake ashes are 1-2 orders of magnitude lower than those in the Finnish recommendation. However, as the production of ash increases, its reuse would need a clear and shared regulation within the European Community (Bonanno et al., 2013).

The TSC of the ashes was similar, 298 and $312 \text{ g CO}_2 \text{ kg}^{-1}$ for FBA and BBA, respectively (Table 1). These values are similar to values reported by Bobicki et al. (2012 for maximum carbonation of several waste products. Nevertheless, it should be considered that K and Na carbonates are highly soluble in water and that the TSC attributable to these compounds should not be taken into account in the case where the ashes are applied as soil fertilizer or amendment. For this reason, the TSC-(Ca+Mg) of our ashes is reduced to 154 and $236 \text{ g CO}_2 \text{ kg}^{-1}$ for FBA and BBA, respectively. The actual carbonate content in FBA and BBA was 74.9 and $48.9 \text{ g CO}_2 \text{ kg}^{-1}$, respectively, which indicates that carbonation has been completed to 25.1% (FBA) and 15.7%

(BBA) of the total-TSC or to 48.7% (FBA) and 20.8% (BBA) in relation to TSC-
(Ca+Mg). The BBA ash was wetted at the factory to a moisture content of 315 g
kg⁻¹ (Table 1). Generally, water promotes the carbonation reaction with CO₂,
and the value 0.3 water/solid ratio has been reported as optimum for a
municipal solid waste ash (Bobicki et al., 2012). In the case of FBA, despite its
low moisture content (Table 1), this was carbonated to a larger extent than
BBA. Vassilev et al. (2013b) indicate that CO₂ from flue emissions of biomass-
fired power plants can be partially captured and retained in fly (and in bottom)
ashes as carbonates, and even atmospheric CO₂ is captured by Ca, K, Mg and
Na oxides and other chemical compounds contained in the combustion residues
during their storage and weathering. In our case, the greater CO₂ content in
FBA could be due to the small size of FBA stockpile which favoured CO₂
diffusion, or to the particular FBA chemical composition.

3.2. Incubation experiment

A summary of results corresponding to the incubation experiment is shown
in Table 2. At the start of the experiment with the model soil (day -25), the pH of
soil mixtures containing FBA was alkaline (9.5) and higher than in BBA-based
soil (8.8), and the E.C. was twice that in BBAs. During the 25-day period before
plant seedling, the pH for both treatments FBAs and BBAs increased to 10.1
and 9.8, respectively, while soil E.C. decreased to 1.3 dS m⁻¹ in FBAs and 0.5
dS m⁻¹ in BBAs. At the end of the growing period (day 84), the pH dropped to
values close to neutral in the range of 7.23 to 7.91, which can be considered as
similar or slightly lower than usual values in calcareous agricultural soils.

Differences in pH among the treatments were not significant. The E.C. dropped to values in the range 0.3-0.7 dS m⁻¹. These results were in accordance with previous research of Quirantes et al. (2016, who find that pH is not affected when a calcareous soil is incubated with up to 25 Mg ha⁻¹ of olive cake ash, and this is also accordance with research by Nogales et al. (2006).

There was total sunflower germination in BBAs, but only 67% of the seeds germinated in FBAs. The higher pH, the high salinity or the combined effect of both parameters likely inhibited seed germination in FBAs. After germination, the plants grew in good condition in both treatments. Approximately half way the experimental period the remaining plants in FBAs withered, despite the reduction of pH and E.C. observed during the growing period in that treatment. Likely, salts leached and accumulated into the bottom of the pots, affecting plant roots. In BBAs, the plants stopped growing because of being constrained by the small volume of the pot which, consequently, led to their finishing the growing period. Despite these drawbacks, it should be taken into consideration that this experiment was not specifically designed to study the agronomical effects of BAs that were used in much higher doses than the plant fertilizer requirements.

Recovery of the different soil fractions at the end of the incubation experiment are shown in Table 2. Most of the coarser components, i.e., limestone (> 2 mm) and sand (0.5-2 mm), were almost totally recovered. The recoveries of the fraction > 2 mm tended to be slightly lower than 100% while for the particles ranging 0.5-2 mm they tended to be slightly higher than 100%. However, the finest fraction (< 0.5 mm), including peat and BA, was not totally recovered. Hence, the weight of the finest fraction (<0.5 mm) did not seem to

increase due to particles from the breakage of the coarser fractions. The weight loss in this fine fraction could be attributed to i) peat organic matter dissolution favoured by the alkaline pH of the soil which could be inferred from the brown colour of the soil solution; ii) organic matter degradation; iii) aggregation of fine particles with coarser particles or iv) changes in the inorganic chemical compounds of the ashes.

3.3. Stable isotopes composition

Stable carbon isotope composition ($\delta^{13}\text{C}$) measured in the soil constituents and in the finely-sized fraction ($<0.5\text{ mm}$) of the soils of the incubation experiment at the end of the growing period are shown in Table 3. The $\delta^{13}\text{C}$ value for BBA was higher than that of FBA, probably indicating that carbonation process in FBA took place closer to the flue gas while in the case of BBA, a portion of ^{13}C -enriched atmospheric CO_2 could be captured during combustion. In the soils, we were unable to detect any effect of the presence of plants during the incubation experiment since the differences among each pair, with and without plants, were negligible. Actual values of $\delta^{13}\text{C}$ in the soils agreed with the calculated values using the corresponding initial $\delta^{13}\text{C}$ values of the soil components and their ratio in each treatment. As expected, $\delta^{13}\text{C}$ values of atmospheric- CO_2 and limestone were higher than those measured in the soil components. If atmospheric CO_2 would have been mineralized and incorporated into soil that would have increased $\delta^{13}\text{C}$ in 0.2‰ per each 1% atmospheric CO_2 absorbed. The obtained values were very similar to $\delta^{13}\text{C}$ values obtained by Anders Ohlsson (2000) in the surface of ash granules

deposited on a forest soil after a short incubation period. This author also indicated that the contribution of atmospheric CO₂ could be negligible. Similarly, if weathering or abrasion of coarser limestone pebbles would have been transferred to the fine-sized fraction, that would have increased $\delta^{13}\text{C}$ in 0.3‰ per each 1% CaCO₃ transferred. Hence, it could be concluded that: i) there are no signs of CO₂ fixation from the air during the soil incubation in any of the ash-amended soils, and ii) there are no signs of sample contamination originating from the limestone.

3.4. TGA-DTG

The results of TGA of the soil components, as well as the corresponding DTG plots for limestone, peat and compost, are shown in Fig. 1. The DTG plot for peat shows a peak about 70 °C (peak A), a very sharp peak at 273 °C (B) and a smaller peak (C) at 383 °C. According to the possible physico-chemical transformations during biomass combustion indicated by Vassilev et al. (2013c and Fernández et al. (2012, these peaks could be attributed to water evaporation (A), decomposition of hemicelluloses (B), and decomposition/oxidation of cellulose (C).

The DTG plot for limestone shows a sharp peak at 600-800 °C (peak E). This peak likely corresponded to decarbonation of Ca carbonate to lime. Vassilev et al. (2013c assigned temperatures in the range of 500-900 °C to the decarbonation process of carbonates.

Peaks in similar positions to A, B and C peaks of peat appeared for the raw ingredient compost though their intensity was rather low (look at the

corresponding DTG axis scale in Fig. 1). The DTG for compost also shows two additional peaks at 429 °C (D) and 655 °C (E). Peak D could correspond to the decomposition of lignin (Fernández et al., 2012; Vassilev et al., 2013c). The peak E could correspond to the decarbonation process of a small amount of carbonates formed from the plant nutrients Na, K, Ca, Mg in the compost.

The results of the TGA corresponding to FBAs-pl fine soil fraction as well as its corresponding DTG plot, and the DTG plot for FBA are shown in Fig. 2. The DTG profile for FBAs-pl shows peaks in the temperature range 270-430 °C, similar to the peaks B and C of peat and D of compost. The sharp peaks in the temperature range of 270-430 °C could be due to more stabilized organic matter fractions originating from peat degradation during the growing period or, alternatively, to the interaction of SOM with metallic divalent cations. At a temperature above 600 °C, a peak is present in both FBAs-pl and in the FBA. This peak is located near peak E of limestone (Fig. 1) and, consequently, could be attributable to calcite decarbonation. Finally, between 800 and 900 °C, the DTG shows a small change (peak F). Dolomite ($\text{CaMg}(\text{CO}_3)_2$) is known to be decarbonated in a two-stage process: firstly, MgCO_3 forms MgO at 650–750 °C and secondly, CaCO_3 part is decomposed to CaO at 800–900 °C (Vassilev et al., 2013c). In accordance with FBA composition (Table 1), it is likely that dolomite would be present in FBA composition, hence, peaks E and F would correspond to dolomite decarbonation. Nevertheless, peaks in the region near 900 °C, when constant weight is reached, have also been assigned to the stage of char oxidation or combustion of carbonaceous residue without flame (Fernández et al., 2012). As ashes contain organic-C (Table 1), the peak F could also in part correspond to this carbonaceous fraction. The corresponding

TGA and DTG plots for the treatment FBAs-no were similar to those in Fig. 2, hence, the corresponding figure for that treatment is not shown.

The results of the TGA of BBAs-pl fine soil fraction, as well as its corresponding DTG plot, and the DTG plot for BBA are shown in Fig. 3. The DTG plot for the treatment BBAs-pl shows peaks A, B, C and D, assigned to moisture and decomposition of the different forms of organic matter. In the region above 600 °C, only peak E is clearly noticeable. A peak at a similar temperature to that of E is also present in the plot for BBA and is attributed to calcite decarbonation. It is noteworthy that, despite peak E also being present in the compost used as feedstock (Fig. 1), its intensity in the compost and the low ratio of compost in the mixtures does not make it feasible to relate this E peak in the treatments to compost. The corresponding TGA and DTG plots for the BBAs-no treatment is very similar to that of BBAs-pl in Fig. 3, hence, the corresponding figure for that treatment is not shown.

3.5. CO₂ fixation

An estimation of the amount of CO₂ fixed at the end of the trial in the fine fraction (< 0.5 mm) sieved from each soil is shown in Table 4. Two approaches were used for the calculation. The first approach makes use of the total carbonate content, determined by means of the calcimeter method after correction by the weight loss corresponding to peak A in TGA (that is about 5.5% moisture content). By using this, a fixed carbonate content corresponding to 14.5 g CO₂ kg⁻¹ was obtained for both FBAs-pl and FBAs-no. The short period of time while plants survived in FBAs-pl did not seem to affect the CO₂

fixed in this soil. In BBAs-pl, CO₂ fixation was significantly greater (16.5 g CO₂ kg⁻¹) than in treatments FBAs and this figure was increased even higher in the treatment without plants (BBAs-no, 19.7 g CO₂ kg⁻¹). The plant roots, due to acid exudates or due to root respiration forming carbonic acid (Berner et al., 2003) could have favoured the releasing of a fraction of the CO₂ from the BBA carbonates. If the actual recovery of the considered (< 0.5 mm) particle size fraction (Table 2) was included in the calculations, the absolute amounts, which are shown in Table 4 as CaCO₃ content per pot, follow the same trend as for the indicated CO₂ content.

In Table 4, the CO₂ content in the fine fraction of the soils is also referred to in the initial weight of ash in the pots (1.8 g per pot) and, following this, the fixed CO₂ on each treatment was expressed as a percentage of the TSC-(Ca+Mg). The TSC-K and TSC-Na are not considered because their CO₂ uptake and weathering are balanced during their geochemical cycles (Garrels, 1983). In FBAs treatments, 24.9-28.0% CO₂ was fixed after incubation, without significant differences, likely due to the short period of plant growth. These percentages decrease from the effective CO₂ initially sequestered in FBA, by 48.7% (Table 1). This decrease in FBA fixation capacity could be due to the contribution of the K carbonate in FBA (look at high K₂O content and TSC-K in FBA, Table 1) which would have been dissolved by irrigation water during soil incubation.

In the case of BBA treatments, 22.2% of TSC-(Ca+Mg) has been reached in the treatment BBAs-pl, a very close value to the initial 20.8% in BBA (Table 1). Apparently, ash BBA has not been significantly altered during plant growth. In the case of BBAs-no, the percentage of CO₂ fixed was significantly higher (27.7%). That is, carbonation process continued in BBA during the incubation

without plant cultivation. As the actual $\delta^{13}\text{C}$ of treatment BBAs-no was not significantly different from its calculated value (Table 3), the additional CO_2 incorporated to BBA could have originated from peat decomposition rather than from the atmospheric air.

The second approach used to calculate CO_2 fixation makes use of the weight loss observed in TGA analyses between 570-700 °C and 590-700 °C in treatments FBAs and BBAs, respectively. Assuming that weight loss was due to decarbonation, the corresponding contents of CO_2 in the incubated soils (Table 4) follow the same trend indicated previously (CO_2 content in FBAs-pl=FBAs-no<BBAs-pl<BBAs-no). Notwithstanding, these results are 40-60% greater than those calculated making use of calcimeter determinations. Thus, it can be concluded that the estimates of CO_2 sequestering when calculated making use of the first approach (38.4 to 65.3 g CO_2 kg⁻¹ ash) can be considered as a conservative approach. These values are similar to carbonate removal capacity of coal fly ash reported by other researchers (26 to 70 g CO_2 kg⁻¹ ash) (Lim et al., 2012; Montes-Hernández et al., 2009) despite these values were obtained under different incubation conditions. To the authors knowledge there are not previous quantitative studies showing the CO_2 fixation of biomass ash treated soils with the exception of that of Anders Ohlsson (2000) which incubated ash granules on the top of an acidic mor layer of a forest soil.

3.6. General comment

The geochemical Ca and Mg cycle can be summarised as follows: i) chemical weathering of Ca and Mg rocks (silicates and carbonates, the latter

being CO₂ neutral on geological timescales); ii) temporary storage of Ca and Mg cations in plants and soils; iii) Ca and Mg moving by streams to the sea; iv) precipitation of carbonate minerals fixing atmospheric CO₂ and sedimentation in the sea; v) retransformation back to silicate rocks by metamorphism and magmatism. This process occurs in nature over thousands of years and exerts a major control on atmospheric CO₂ over long periods of geological time (Berner et al., 2003; Garrels, 1983). Under this scheme, biomass combustion and reutilization of ash in calcareous soils result in a short-circuit avoiding step iii) and most of step iv) and increasing the storage of mineral carbonate forms in the soil. Consequently, the first achievement of the mineral carbon sequestration using BA is an acceleration of the carbonation processes.

To put the level of the CO₂ fixation achieved by ash into perspective, we make comparisons with the objectives of the 'Soil carbon 4 per mille' initiative. The '4 per mille Soils for Food Security and Climate' is an ambitious international research programme that was launched at the COP21 with an aspiration to increase global soil organic matter stocks by 4 per 1000 (or 0.4%) per year as a compensation for the global emissions of greenhouse gases by anthropogenic sources (Minasny et al., 2017). Globally, it could be estimated that, on average, 4 per mille increase equates to a sequestration rate of 0.6 Mg of C per ha per year (2200 kg CO₂ ha⁻¹ y⁻¹).

It can be considered that crop fertilization adding 1 Mg ha⁻¹ of BA-based fertilizer (160 to 307 kg K₂O, depending on BBA:FBA ratio) would be a standard fertilizer dose for most crops. This fertilization rate would annually sequester 38.4 to 65.3 kg CO₂ ha⁻¹ (that is a conservative estimate for FBA and BBA,

respectively) in carbonate forms, which represents 1.7- 3.0% (2.3% on average) of the '4 per mille' target.

Both ashes also contain a significant content of organic C, similar to biochar (Table 1), which adds organic resilient C forms to the inorganic-C sequestering. It is usual that the combustion of biomass material can contain traces of charcoal (Scheepers and du Toit, 2016). Because biochar is mostly non-digestible for microorganisms, it could serve as a permanent, low cycling, carbon-sequestration agent in soils for thousands of years (Lee et al., 2010). This organic black-C would annually represent 1.5-9.5% (5.5% on average) of the '4 per mille' target.

The proposed use of BA is not a minor achievement, since it could reach, per year, 3.2-12.5% (7.9% on average) of the '4 per mille' goal in considering only crop K fertilisation. Moreover, BA fertilization could be used in combination with other recommended management practices as co-application of inorganic ashes and organic amendments (Ram and Masto, 2014). Furthermore, the same BFA used in the present study has been blended with other organic residues (53% BFA) and the resulting product has been used successfully to fertilize crops while maintaining yields (López et al., 2016).

Although, to conduct a complete Life Cycle Assessment is not the objective of the present study, and it would be worth expanding on certain related points about that subject. In a recent paper dealing with bioenergy with carbon capture and storage (BECCS), Fajardy and Mac Dowell (2017) conclude that the most important leakages in BECCS efficiency were chemicals for bioenergy crops, road transport, drying and grinding. The residue covered by the current study, olive cake, shows inherent characteristics which could reduce the carbon

footprint of its energy use because i) it is a dry material, ii) it is previously grinded for oil extraction, iii) it is processed in medium- to large-size factories which concentrate the feedstock, avoiding long transport distances, and finally, iv) the ash could be reused to reduce economic and fertilizer energy costs in the nearby agronomical crops, avoiding chemicals and the corresponding transport costs.

The carbon footprint of the replaced potash fertilizer could amount to 160 kg CO₂ ha⁻¹, equivalent to an additional 7.3% of the 4 per mile target (assuming 1 Mg ha⁻¹ ash amendment, 25% K₂O content in ash, 0.64 kg CO₂-eq kg⁻¹ potash fertilizer Carbon Footprint (Fajardy and Mac Dowell, 2017)).

4. Conclusions

The present results show that the reutilization of ash originated in the combustion of K-rich residues as fertilizer in calcareous soils, guarantees permanent sequestering as carbonate of extra CO₂ to that already saved by biomass power generation, and this will improve the carbon balance of the whole process. This inorganic carbon sequestering practice could add resilience to the current soil organic carbon goals fostered by international programmes. Best management practices for the agricultural use of this type of ash, as well as regulations allowing their blending in fertilisers, should be developed as well as studies considering the carbonation process over a longer period of time should be carried out.

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Figure captions

Fig. 1. TGA-DTG plots for synthetic soil components

Fig. 2. TGA-DTG plots for FBAs-pl and DTG plot for FBA (FBA, fly biomass ash)

Fig. 3. TGA-DTG plots for BBAs-pl and DTG plot for BBA (BBA, biomass bottom ash)

Table 4 CO₂ fixation after the incubation experiment determined following two analytical approaches

	FBA-s-pl ¹	FBA-s-no ²	BBA-s-pl ³	BBA-s-no ⁴
Fraction <0.5 mm				
Calcimeter method				
CaCO ₃ g kg ⁻¹	32.9 (2.1)	32.8 (1.9)	37.6 (2.5)	44.7 (1.1)
CaCO ₃ mg pot ⁻¹	157 (10)	176 (15)	214 (18)	267 (21)
CO ₂ g kg ⁻¹	14.5 a ⁵	14.4 a ⁵	16.5 b ⁵	19.7 c ⁵
TGA-DTG method				
Weight loss (CO ₂ g kg ⁻¹)	20.6 (4.9)	21.1 (0.5)	26.4 (0.9)	27.2 (0.6)
T range °C	570-707	570-700	590-700	590-700
After calcimeter method, referred to as the initial BA weight (1.8 g)				
CaCO ₃ g kg ⁻¹	87.4 (5.7)	97.9 (8.4)	119.0 (9.9)	148.4 (11.9)
fixed CO ₂ g kg ⁻¹	38.4 (2.5)	43.1 (3.7)	52.3 (4.3)	65.3 (5.2)
% CO ₂ fixed ⁶	24.9	28.0	22.2	27.7
p ⁷	0.082		0.009	

¹Soil with fly biomass ash and plant cultivation; ²Soil with fly biomass ash without plant cultivation; ³Soil with biomass bottom ash and plant cultivation;

⁴Soil with biomass bottom ash without plant cultivation;

⁵ Comparison of means following the Tukey HSD test: values in the row followed by the same letter are not statistically different;

⁶Percentage in relation to CO₂ theoretical sequestration capacity due to Ca and Mg (TSC-(Ca+Mg) in Table 2;

⁷ Significance of independent samples t-test comparing the two treatments using the same type of ash.

Values in brackets are standard deviations.

Table 1 Characterization of ashes

		FBA ¹	BBA ²
Moisture	g kg ⁻¹	5.5	315
pH ext 1:5		12.7 ± 0.1	12.8 ± 0.2
EC ext 1:5	mS cm ⁻¹	37.2 ± 0.3	13.3 ± 0.2
organic-C	g kg ⁻¹	8.7 ± 1.7	56.7 ± 0.6
Ca (as CaO)	g kg ⁻¹	99.8 ± 3.9	198 ± 1
Mg (as MgO)	g kg ⁻¹	83.6 ± 3.7	75.2 ± 5.5
K (as K ₂ O)	g kg ⁻¹	307 ± 14	160 ± 2
Na (as Na ₂ O)	g kg ⁻¹	4.78 ± 0.29	3.79 ± 0.40
S (as SO ₃)	g kg ⁻¹	28.4 ± 1.5	3.56 ± 0.13
P (as P ₂ O ₅)	g kg ⁻¹	36.9 ± 1.7	35.3 ± 1.7
CaCO ₃ (calcimeter)	g kg ⁻¹	170 ± 4	111 ± 4
CO ₂ (calcimeter)	g kg ⁻¹	74.9 ± 1.5	48.9 ± 1.8
TSC ³ following the Stenoir stoichiometric formula			
TSC-Ca	g CO ₂ kg ⁻¹	62.8 ± 3.7	154 ± 1
TSC-Mg	g CO ₂ kg ⁻¹	91.2 ± 4.1	82.0 ± 6.0
TSC-K	g CO ₂ kg ⁻¹	141 ± 6.3	73.5 ± 1.1
TSC-Na	g CO ₂ kg ⁻¹	3.4 ± 0.2	2.7 ± 0.3
TSC-(Ca+Mg)	g CO ₂ kg ⁻¹	154 ± 8	236 ± 7
Total-TSC	g CO ₂ kg ⁻¹	298 ± 14	312 ± 8
Effective CO ₂ sequestered (% of TSC)			
% of Total-TSC	%	25.1 ± 1.2	15.7 ± 0.3
% of TSC-(Ca+Mg)	%	48.7 ± 2.5	20.8 ± 0.4
Trace metals			
As	mg kg ⁻¹	4.90 ± 0.76	2.56 ± 0.72
Cd	mg kg ⁻¹	0.46 ± 0.04	0.30 ± 0.04
Co	mg kg ⁻¹	6.48 ± 0.44	7.44 ± 0.24
Cr	mg kg ⁻¹	61.0 ± 4.5	68.1 ± 2.0
Cu	mg kg ⁻¹	171 ± 9	140 ± 6
Hg	mg kg ⁻¹	0.42 ± 0.01	0.30 ± 0.08
Mn	mg kg ⁻¹	391 ± 26	409 ± 26
Ni	mg kg ⁻¹	55.0 ± 3.3	60.3 ± 1.1
Pb	mg kg ⁻¹	9.94 ± 0.61	2.51 ± 0.95
Zn	mg kg ⁻¹	195 ± 9	49.6 ± 3.0

¹ FBA: Fly biomass ash; ² BBA: Biomass bottom ash;³ TSC: Theoretical sequestration capacity

Table 2 Summary of results of the incubation experiment

	FBAs-pl		FBAs-no		BBAs-pl		BBAs-no	
	Recovery (%) by particle size (%)							
All	99.1	(0.26)	99.3	(0.13)	99.2	(0.15)	99.5	(0.02)
F>2 mm	99.3	(1.42)	99.7	(0.44)	99.6	(0.48)	99.6	(0.18)
F 0.5-2 mm	100.2	(0.54)	100.2	(0.08)	100.0	(0.25)	100.2	(0.12)
F<0.5 mm	57.8	(5.3)	65.7	(4.4)	68.7	(6.2)	71.8	(4.2)
	pH evolution							
pH day -25	9.54	(0.1)	9.54	(0.1)	8.79	(0.1)	8.79	(0.1)
pH day 0	10.11	(0.1)	10.11	(0.1)	9.80	(0.2)	9.80	(0.2)
pH day 84	7.73	(0.4)	7.91	(0.3)	7.23	(0.3)	7.68	(0.5)
	Electrical conductivity (dS m ⁻¹) evolution							
E.C. day -25	1.99	(0.05)	1.99	(0.05)	1.02	(0.04)	1.02	(0.04)
E.C. day 0	1.32	(0.36)	1.32	(0.36)	0.51	(0.14)	0.51	(0.14)
E.C. day 84	0.31	(0.38)	0.69	(0.24)	0.36	(0.14)	0.67	(0.17)
	Germination (%)							
Day 10	63		-		100		-	
	Plant height (cm)							
Day 10	7.9	(3.1)	-	-	11.2	(3.9)	-	-
	Dry plant biomass (g plant ⁻¹)							
Day 84	-	-	-	-	1.78	(0.18)	-	-

¹FBA: Fly biomass ash; ²BBA: Biomass bottom ash;

Values in brackets are standard deviations.

Table 3 $\delta^{13}\text{C}$ in the soils and the soil components

	$\delta^{13}\text{C}$	sd ⁴	$\delta^{13}\text{C-calc}$ ⁵
Components			
Peat	-25.9	0.1	
Compost	-26.6	0.2	
FBA ¹	-25.6	0.5	
BBA ²	-23.6	0.2	
Limestone	1.4	0.2	
Atm-CO ₂ ³	-8.6		
Soils			
FBA-s-pl	-26.1	0.3	-25.9
FBA-s-no	-25.9	0.1	-25.9
BBA-s-pl	-25.7	0.1	-25.5
BBA-s-no	-25.6	0.4	-25.5

¹FBA: Fly biomass ash; ²BBA: Biomass bottom ash;

³ Average value for 2014 measured in Centro de Investigación de la Baja Atmosfera (CIBA), Spain (White et al., 2015)

⁴sd: standard deviation n=4

⁵ $\delta^{13}\text{C}$ calculated from the starting components

Table 4 CO₂ fixation after the incubation experiment determined following two analytical approaches

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