Thermal analysis of aged chars obtained by pyrolysis and hydrothermal carbonisation of manure wastes

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Thermal analysis of aged chars obtained by pyrolysis and hydrothermal carbonisation of manure wastes

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Abstract

Biochar is being explored for the improvement of contaminated land as well as quality of soils in agricultural use. Most studies are conducted in the laboratory or involved only short-term field experiments. There remains considerable uncertainty about the long-term implications of biochar use, as a consequence of changes that arise during their ageing within soil. This work assessed the effects of chemical ageing (5% vol H_2O_2) on different properties of biochars and hydrochars prepared from two types of animal waste (rabbit and pig manure). Four biochars were prepared from pyrolysis of rabbit manure (pyrolysis temperature: 300 and 600 °C) and pig manure (300 and 450 °C) and two hydrochars from each manure by hydrothermal carbonisation at temperatures of 200 and 220 °C. The pristine and aged chars were compared according to the elemental composition and thermogravimetric analysis being also calculated the thermostability index and carbon stability in the ageing process. Results showed that chars prepared at lower temperatures were more sensitive to ageing. Only biochar obtained by pyrolysis at 600 °C showed a high level of resistance to ageing, reflecting the higher stability of the underlying carbon structure.

Keywords Pyrolysis · Hydrothermal carbonisation · Biochar · Carbon stability · Thermogravimetry

Introduction

The generation of huge amounts of manure wastes can result in serious changes in their management and disposal. Animal farming produced approximately 1.4 Gt of manure per year from 2016 to 2019 in the EU-27 and UK [1]. These wastes are rich in organic carbon, nitrogen, phosphorus and other elements, including Ca, Mg, Fe, Zn or Cu, and traditionally have been used directly as soil amendments. However, land application of manures leads to deleterious environmental outcomes including greenhouse gas emissions, air and water pollution, heavy metal pollution and pathogen transmission [2]. For example, phosphorus and nitrogen in manure lead to water eutrophication and air pollution arises from the presence of reactive nitrogen-containing compounds (emissions of ammonia and the greenhouse gas nitrous oxide). Additionally, the presence of hormones, antibiotics, pathogenic bacteria or trace metals in manures limits its application to land, due to potential negative effects on environmental sustainability and public health [3]. However, proper transformation of manures can make these wastes interesting raw materials for the sustainable management of land and waste within a circular economy [4].

Producing biochar from manure waste and its soil application could be an alternative of waste valorisation, which can improve soil properties while reducing the risk of their direct soil use and building soil carbon [5]. Biochar (also known as pyrochar) is a carbon product produced by biomass thermal treatment (300–700 °C) under the conditions of limited oxygen atmosphere. The recalcitrance of biochar leads to avoided emissions of CO_2, creating a long-term sink for plant-derived carbon [6]. Manure wastes is used as material for biochar production; however, drying manures with high water content such as pig slurry has economic,

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logistical and life-cycle implications. For this reason, hydrothermal carbonisation (HTC) with production of hydrochar can be an economical option for wet manures. HTC is done in water solution, using lower temperatures (180–260 °C) than pyrolysis and under autogenous pressure [7]. The aqueous product remaining after recovery of hydrochar could be recycled through HTC or used as fertiliser, resulting in lower net energy consumption and fewer effluents compared to thermal pyrolysis.

The structure, composition and possible uses of biochars and hydrochars differ [8]. Both can act as CO_2 sinks due to their stability [9, 10]. However, physicochemical properties of chars can undergo important changes when added to soils as a result of different biotic and abiotic processes, usually termed "ageing" [11]. Ageing of biochars or hydrochars in natural conditions is a long-term process. For this reason, different techniques have been used for controlling conditions to simulate long-term effects of environmental factors on chars and accelerating their decomposition [12–14]. According to Wang et al. [15], the artificial ageing methods can be classified into chemical oxidation (chemical ageing), physical ageing and biological ageing. Chemical ageing implies the changes in chemical functional groups on char surfaces and the common approaches for this type of ageing process are organic acid-induced ageing that feigns root exudates, chemical oxidation that simulates the influence of inorganic ions and photocatalytic oxidation that mimics sunlight irradiation. The physical ageing involves changes in morphology due to two principal factors: temperature and moisture, and for that reason, the use of freeze and wet thaw cycling. In the case of biological ageing, it is related to microbial degradation effects and can be artificially accelerated by co-composting an anaerobic fermentation [15]. Controlled addition of hydrogen peroxide (H_2O_2) on biochars has been used as a rapid analogue to study the effect of oxidation over extended periods in soils; also, the peroxide is commonly used as oxidant that can simulate natural oxidation process [12]. While the physicochemical properties of pristine and ageing biochars have been more studied, the ageing of hydrochars remain less analysed. The objective of this paper is to compare the hydrogen peroxide ageing on hydrochars and biochars obtained after HTC and pyrolysis of manure wastes.

Materials and methods

Feedstock selection and char preparation

Two manures were selected as raw material for the preparation of eight chars: rabbit manure (RM) and pig manure (PM). RM was provided by an experimental rabbit farm (Universidad Politécnica de Madrid, Spain), whereas PM was obtained from a pig farm (Ávila, Spain). Samples were air-dried for 3 months and sieved under 5 mm.

The four biochars were obtained as follows: 500 g of RM or PM was placed in a 2-L steel reactor. Manures were heated at 3 °C min^{-1} until the pyrolysis temperature was maintained for 3 h. Inert atmosphere was achieved with a N_2 flow of 0.5 L min^{-1}. For RM, pyrolysis temperatures were 300 and 600 °C, leading to BRM300 and BRM600, respectively, whereas for PM material, pyrolysis temperatures were 300 and 450 °C, leading to BPM300 and BPM450, respectively.

The four hydrochars were obtained as follows: 1.0 L of wet MW solution with 30% solid content was introduced in a Hastelloy autoclave. Both raw materials (RM or PM) were heated at 200 and 220 °C, maintaining the final temperature for 6 h. After that, the final solutions were filtered. Then, the solid sample was dried at 90 °C (24 h) and sieved. Hydrochars were named as HRM200 and HRM220 for RM waste and HPM200 and HPM220 for PM waste treated at 200 or 220 °C, respectively.

Characterisation of samples

Pristine and aged chars were characterised as follows:

Elemental analysis was determined by dry combustion with a LECO CHNS-932 analyser (SCAI-Málaga University, Spain). Oxygen content was obtained by difference as 100 % − (%C + %H + %N + %S + %Ash). The results were used to obtain the atomic ratios H/C and O/C.

Thermogravimetric analysis was carried out in a Labsys Setaram thermogravimetric analyser for both aged and pristine chars. Twenty milligrams of each sample was heated until 850 °C (heat rate: 15 °C min^{-1}) in air atmosphere (flow rate: 30 mL min^{-1}). Thermogravimetric results were calculated as the sample mass loss at different temperature ranges: WL1 (range: 25–150 °C), WL2 (200–400 °C) and WL3 (400–600 °C) [16]. WL1 is associated with sample water release, while WL2 and WL3 are related to mass loss due to organic matter combustion. The first peak (WL2) corresponds to the combustion of less humified or more immature organic matter, while the second one (WL3) is related to more humified or complex organic matter [16, 17]. The thermostability index (WL3/WL2 ratio) is a credible parameter usually used to study the organic matter stability of in biochars, composts or other organic wastes [16, 18]. This index is the ratio between more stable organic matter with respect to the less humified organic matter.

Carbon stability in the ageing process (CAS) was assessed for biochars and hydrochars, calculated on the basis of mass loss and the carbon content of the sample, according to the following equation [12]:

$$CAS(\%) = \frac{C_r \times C_{rC}}{C_t \times C_{tC}} \times 100$$

where

CAS is the carbon ageing stability (%).

C_r is the residual mass of pyrochar or hydrochar post-ageing.

C_{rC} is the C content.

C_t is the initial mass of pyrochar or hydrochar prior to treatment.

C_{tC} is the C content of pyrochar or hydrochar freshly produced.

Results and discussion

Table 1 shows the elemental analysis, H/C and O/C ratios of the pristine and aged chars. The percentages of C range between 25 and 30% for pristine chars and 4–17% for aged chars. In all cases, the carbon content decreased with the artificial ageing process, indicating that samples contain labile and more readily oxidised carbon removed during the oxidation with H_2O_2 [19, 20]. This result was according to other authors that used different ageing processes [12, 21]. BRM600 obtained at the highest pyrolysis temperatures leads to aged sample with the highest carbon content. This result is indicative of high biochar stability due to high pyrolysis temperatures used in their preparation and is according to previous works, which concluded that manure waste pyrochar (pyrolysis temperature; 600 °C) had a high biological, chemical and thermal stability [8]. Other researchers have previously found that biochars produced from sewage sludge at 700 °C showed lower changes in C content during ageing, supporting the relationship between pyrolysis temperature and carbon stability [22].

The hydrogen, nitrogen and sulphur contents were lower in aged samples than in pristine chars reaching values lower than the detection limit for sulphur. In the case of oxygen, their content decreased after ageing of chars except for BRM600 that increased the oxygen content from 0.99% for pristine (BRM600-pri) to 14.37% for aged (BRM600-ag). Dong et al. [23] found a decrease in oxygen content in aged biochar attributed to dissolution or decomposition of organic labile compounds [13, 23]. Difference in the case of BRM600 could be related to the highest stability of carbon structures more resistant to oxidation and where the H_2O_2 leads to the formation of oxygenated groups increasing their oxygen content of char surface. H/C and O/C ratios varied with ageing treatment and show a specific trend with lower ratios for the pristine chars that increased for ageing samples [24], except for HPM200-ag. Van Krevelen diagram is shown in Fig. 1. It can be observed how the biochars prepared between 300 and 450 °C and hydrochars obtained by HTC at 200 or 220 °C are found in close regions in the van Krevelen diagram. After ageing with H_2O_2, chars show a greater dispersion, which indicates that although they present similar values of H/C and O/C, their behaviour during ageing process may be very different. The trend is that, after the ageing process, the ratios O/C and H/C increase, showing a reduction in the stability after the simulation of the degradation of chars. This fact occurred for 3 biochars (BPM450-ag, BPM300-ag and BRM300-ag) and 3 hydrochars (HPM220-ag, HRM200-ag and HPM220-ag). Nevertheless, The BRM biochar prepared at 600 °C after ageing process (BRM600-ag) was found in the area of van Krevelen diagram with greater aromaticity due to its greater

Table 1 Elemental analysis (C, H, N, S, O), ash content and H/C and O/C ratios for pristine (pri) and aged (ag) biochars and hydrochars

Sample	% C	% H	% N	% S	% Ash	%O	H/C	O/C
BRM300-pri	29.73	3.17	2.03	0.48	50.50	14.09	1.28	0.36
BRM300-ag	5.56	0.74	0.52	0.00	84.25	8.92	1.60	1.20
BRM600-pri	29.41	1.29	0.80	0.38	67.14	0.99	0.53	0.03
BRM600-ag	16.18	0.95	0.86	0.00	67.64	14.37	0.70	0.67
HRM200-pri	29.49	3.38	2.00	0.42	49.47	15.25	1.38	0.39
HRM200-ag	5.92	1.03	0.80	0.00	82.17	10.08	2.09	1.28
HRM220-pri	29.93	3.10	2.00	0.42	48.47	16.09	1.24	0.40
HRM220-ag	6.33	1.09	0.68	0.00	78.19	13.72	2.07	1.63
BPM300-pri	25.71	2.88	1.66	0.44	48.54	20.77	1.35	0.61
BPM300-ag	6.11	1.24	0.62	0.00	79.69	12.33	2.44	1.51
BPM450-pri	27.81	1.35	1.30	0.27	46.56	22.70	0.58	0.61
BPM450-ag	7.90	1.28	0.78	0.00	82.32	7.71	1.95	0.73
HPM200-pri	30.04	3.75	2.21	0.49	44.06	19.45	1.50	0.49
HPM200-ag	9.93	1.78	1.53	0.00	84.30	2.47	2.15	0.19
HPM220-pri	26.39	3.08	1.84	0.52	50.81	17.37	1.40	0.49
HPM220-ag	4.30	0.79	0.41	0.00	86.89	7.61	2.20	1.33

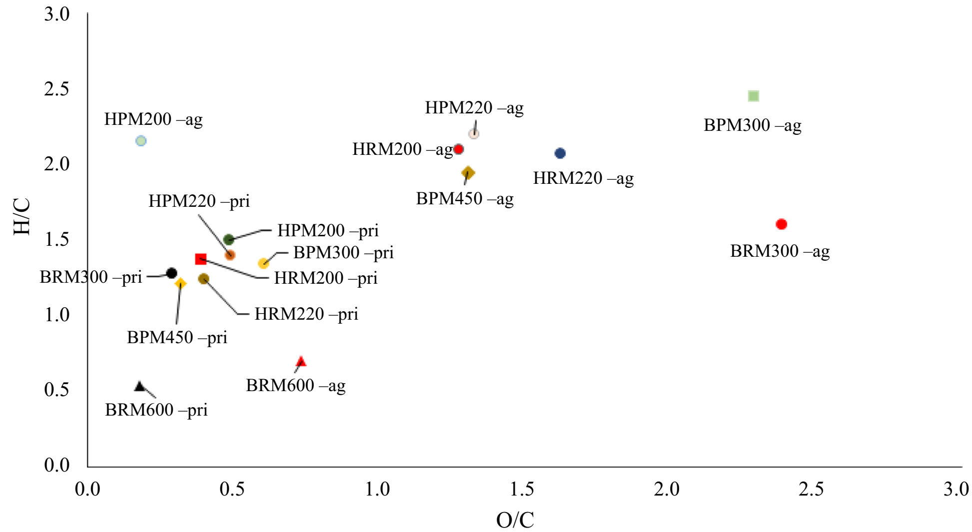

Fig. 1 Van Krevelen diagram for pristine (pri) and aged (ag) biochars and hydrochars

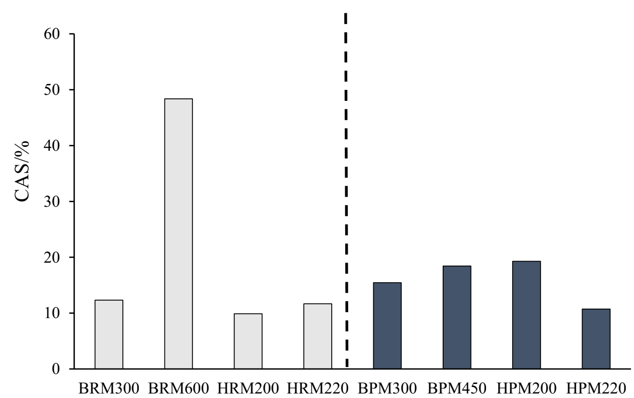

Fig. 2 Carbon stability in the ageing process (CAS) for biochars and hydrochars

stability according to the higher pyrolysis temperature (BRM600-pri).

The percentages of ash content were clearly higher in aged samples (Table 1) due to their enrichment during the ageing process oxidation of carbon structures [19]. It is important to highlight that biochar obtained at 600 °C (BRM600-pri) with the highest initial ash content (67.1%) led to chars with the lowest ash ratio in the aged samples (67.6%) due to higher stability of the carbon structures. Therefore, despite its higher ash content, it hardly increased with time.

Figure 2 represents the percentage of carbon stability in the ageing process (CAS) [12]. The more stable sample was BRM600 with a 48.4%, whereas the rest of the chars produced from rabbit manure exhibited a percentage of carbon stability around 10%. The chars obtained by pyrolysis at 300 and 450 °C or HTC at 200 and 220 °C of pig manure showed percentages between 10 and 20%, with the lowest percentage for the hydrochar HPM220. Pyrolysis temperature has an important role in carbon stability [24] with the highest percentage in the biochar produced at the highest temperatures. Biochars obtained at temperatures between 300 and450 °C show carbon stability values similar to that of hydrochars according to previous works performed by Gascó et al. [25].

Table 2 Thermostability index for pristine (pri) and aged (ag) biochars and hydrochars

Sample	WL1	WL2	WL3	WL3/WL2
BRM300-pri	0.35	2.9	2.8	0.97
BRM300-ag	0.25	1.79	1.43	0.80
BRM600-pri	0.14	0.73	3.66	5.01
BRM600-ag	0.44	1.57	3.96	2.52
HRM200-pri	0.93	4.15	3.92	0.94
HRM200-ag	0.61	1.04	1.3	1.25
HRM220-pri	0.05	2.99	2.94	0.98
HRM220-ag	1.1	2.37	1.74	0.73
BPM300-pri	0.65	2.23	2.48	1.11
BPM300-ag	0.95	2.15	1.9	0.88
BPM450-pri	0.46	2.86	3.81	1.33
BPM450-ag	0.97	2.25	1.77	0.79
HPM200-pri	1.33	3.34	2.36	0.71
HPM200-ag	0.3	0.27	0.23	0.85
HPM220-pri	0.14	2.51	2.24	0.89
HPM220-ag	0.48	0.72	0.83	1.15

Table 2 shows thermostability index of pristine and aged chars obtained by thermogravimetric analysis. Thermal analysis is usually used to the characterisation of carbonaceous materials used as fuels (oil, coal). Also, the ageing of biosolids and biochar from biosolids pyrolysis in soils has been studied by Gascó et al. [18] using thermal analysis. As a general trend, WL2 and WL3 decreased with the ageing

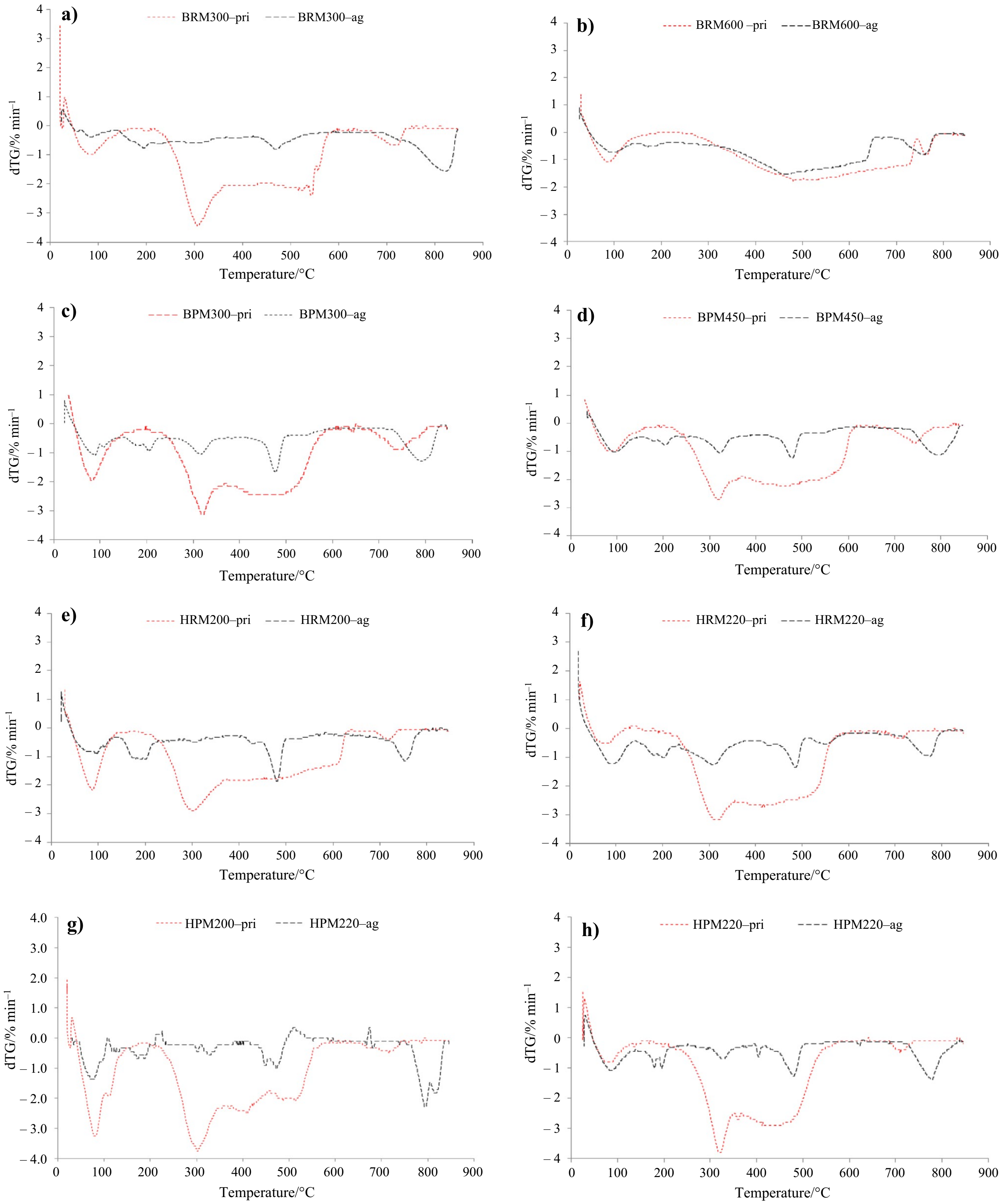

Fig. 3 Derivative of thermogravimetric analysis (dTG) for **a** BRM300, **b** BRM600, **c** BPM300, **d** BPM450, **e** HRM200, **f** HRM220, **g** HPM200, **h** HPM220

of chars (BRM600 being the exception). The WL3/WL2 ratio, related to the thermal stability of the chars, decreased slightly in the case of biochars, while for the hydrochars presented small variations or even slight increases, which means that the aged hydrochars have a greater thermal stability than the original ones.

Figure 3 shows dTGs of pristine and aged chars. The mass loss between 20 and 150 °C is related to water evaporation. Oxidation of organic matter takes place at temperatures from 200 to 550 °C. At temperatures higher than 550 °C, mass loss is attributed to the decomposition of carbon and clays. Finally, carbonate decomposition is observed between 700 and 800 °C [18]. In general, aged chars show less mass loss between 20 and 150 °C, indicating less water adsorbed in their surface. It is interesting to note that dTG curves of aged chars show a new peak at 200 °C that can be related the presence of new light compounds originated during ageing process. Broadbands between 200 and 550 °C were less intense in aged chars compared to pristine ones due to the oxidation of carbon structures. Finally, for aged chars, the peak related to carbonate decomposition increases and shifts to higher temperatures [26, 27].

Conclusions

Ageing of manure waste biochars obtained by pyrolysis at 300 and 450 °C and hydrochars obtained by hydrothermal carbonisation at 200 and 220 °C peak temperatures markedly influenced composition. In contrast, biochar obtained by pyrolysis at 600 °C shows considerable resistance to ageing, reflecting the higher stability of their carbon structures.

Dispersion on a Van-Krevelen diagram increased with ageing of biochars and hydrochars. Although pristine chars have similar values of H/C and O/C, their behaviour during ageing process is different and leads to chars with quite diverse carbon structures.

Thermal analysis of pristine and aged chars could be a key tool to study the impacts of ageing processes in the environment in order to understand and predict their behaviour after soil addition.

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Author contributions All authors contributed to the intellectual input and provided assistance in the study and manuscript preparation.

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