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Hydrochar stability: understanding the role of moisture, time and temperature in its physiochemical changes

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Abstract

Limited information is available about potential physicochemical changes that can occur in hydrochar post-production, e.g. during drying and storage. Understanding these changes is crucial not just for shaping future research plans, but also for future practical applications. Here we studied the effect of moisture (69.2% and 2.4%) and three storage temperatures (− 18, 4, and 20 °C) over a year on selected organic and inorganic compounds in hydrochar produced from the Hydrothermal carbonization (HTC) of digested cow manure. Comparison of the control wet hydrochars (WHs) and dry hydrochars (DHs) showed changes in organic compound composition due to drying. Overall, the total amount of the selected organic compounds was notably greater in WH (15.2 g kg^{−1} DM) compared to DH (11.8 g kg^{−1} DM), with variations observed in individual compound concentrations. Drying, however, had no significant influence on the identified inorganic compounds. Storage caused significant changes in both WH and DH, particularly in organic compounds after 12 weeks. Sugars (2–sevenfold), acids (36–371%), and aromatics (58–120%) in stored samples at week 52 were significantly higher than their control values. Changes in the inorganic elements (e.g., Co, K, Mg, Mn, P, S, Sr, and Zn) occurred faster in WH, with significant differences starting from week 1 compared to their control values, while DH showed fewer changes. Based on these changes in both organic and inorganic content, we recommend the optimal storage conditions for future HTC studies to preserve hydrochar properties. Finally, we discussed potential applications for stored hydrochars, with DH showing greater stability, especially at − 18 °C, making it suitable for various applications.

Highlights

- Drying of hydrochar and storage time affected concentrations of acids, aromatics, and sugars significantly
- Changes were observed at all storage temperatures—dried hydrochar stored at − 18 °C exhibited higher stability.
- Recommended storage conditions could be used for upcoming HTC research and hydrochar applications.

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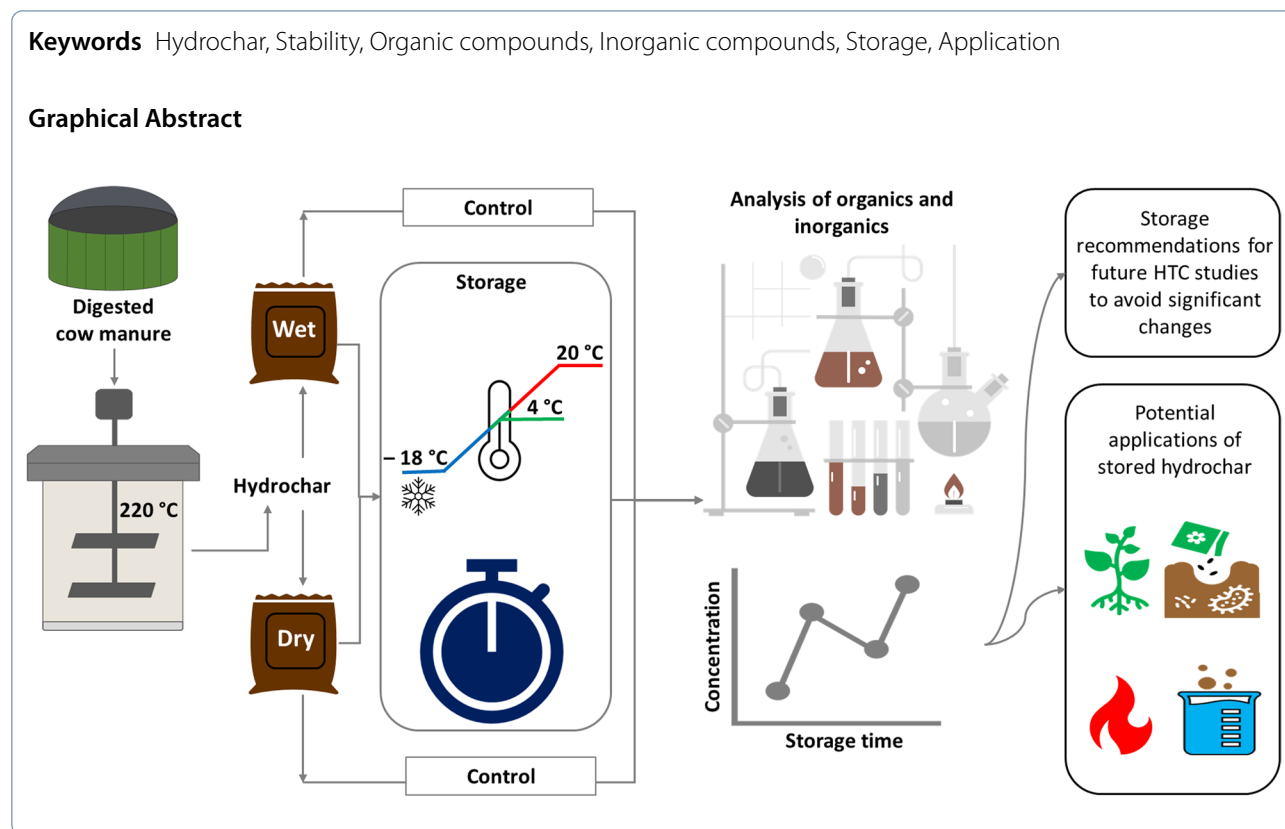
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1 Introduction

Hydrothermal carbonization (HTC) is a sustainable method for converting organic waste into hydrochar, a carbon-rich solid, and has shown its potential for use in different applications, including agriculture (Baronti et al. 2017), environment (Han et al. 2016, 2017), biofuel, and energy production (Berge et al. 2015; Saba et al. 2017). The characteristics of hydrochar, including its elemental composition, surface morphology, functional groups, as well as inorganic and organic content, are significantly influenced by both the feedstock composition and the process conditions of the HTC method. These factors indeed have an effect on the potential applications for the resulting hydrochar (Sivaranjane et al. 2023).

The composition of the feedstock influences the formation of hydrochar during hydrothermal carbonization, which usually takes place in two steps: solid–solid reactions (Fang et al. 2008; Dinjus et al. 2011), and a series of reactions in the liquid phase (Demir-Cakan et al. 2009; Poerschmann et al. 2017). The latter involves conversion of cellulose and hemicellulose to sugars which then form organic acids and lower the pH, leading to the formation of furans (Falco et al. 2011a; Arauzo et al. 2020), which then together with dissolved lignin products [e.g., phenol, catechol, and guaiacol

(Fang et al. 2008)] polycondensate and form hydrochar. Therefore, the hydrochar can contain some of these small organic acids, furfurals, and phenolic compounds (Lucian et al. 2018). In some applications, the presence of these small chain organics can have negative effects on the process, e.g. in adsorption, where they can be washed out into the aqueous phase, and in soil applications, where organic acids (acetic acid) and phenolic compounds (guaiacol and catechol) have been found to affect seed germination and plant growth, particularly root growth (Bargmann et al. 2013). Thus, in order to reduce water soluble carbonaceous compounds, various pre-treatment approaches have been suggested, such as storage and washing (Bargmann et al. 2013) or implementing chemical treatment methods (Fornes and Belda 2017). In addition to the influence of feedstock composition on hydrochar properties, process conditions like pH, time, temperature, and biomass-to-water ratio significantly shape hydrochar characteristics, impacting its practical applications. Notably, temperature emerges as an important parameter affecting key attributes. Higher temperatures enhance the calorific value of the char (often called the higher heating value, HHV) and carbon enrichment of hydrochar, consequently boosting the HHV. Simultaneously, hydrochar

yield decreases with elevated temperatures (Marzban et al. 2022). Furthermore, temperature plays a critical role in developing hydrochar's adsorption capacity. The temperature influence surpassed that of time and the biomass-to-water ratio for determining the adsorption of methylene blue on hydrochar (Akbari et al. 2023). Besides temperature, pH also plays a role, as Reza et al. (2015) noted enhanced porosity and surface area in hydrochars processed at low pH, rendering them more effective adsorbents. Investigating alkaline reaction media, Tkachenko et al. (2022) found that adjusting KOH concentration influenced carbonization, impacting solid yield and carbon content with potential applications in agriculture. Thus, the physicochemical and structural features of hydrochar appear to dictate its prospective applications. Now the question is, what physicochemical changes may occur after the production of hydrochar?

Numerous studies have investigated diverse feedstocks to optimize HTC process conditions for specific applications (Álvarez-Murillo et al. 2015; Sabio et al. 2016; Nizamuddin et al. 2016; Kannan et al. 2017). However, despite these efforts, there is a lack of information concerning the physicochemical changes occurring in hydrochar post-production before its actual application. The HTC process itself is time-consuming, making it challenging to immediately utilize hydrochar for various purposes after production. Consequently, hydrochar may need to be stored before application, which has the potential to alter its intended physicochemical properties. For instance, changes over time have been reported for thermoconversion products such as bio-oils produced from fast pyrolysis of lignocellulosic biomass (Alsobou and Helleur 2014). The high content of reactive oxygen-containing compounds in bio-oils leads to polymerization, increased viscosity, and the formation of water-insoluble products during storage (Oasmaa and Kuoppala 2003). Cooling storage at 5 °C has been found to mitigate changes in viscosity (Elliott et al. 2012). The same instability also was observed in the HTC process liquid. A previous study has shown the changes in organic and inorganic compounds in the HTC process liquid after separation from solid, even at deep freezing temperatures, due to unreacted moieties (e.g., sugars, organic acids, and aromatics) along with undergoing additional reactions (Marzban et al. 2023). Furthermore, stored HTC process liquid was reported to have less inhibitory effect on germination (Bargmann et al. 2013).

Since hydrochar usually contains organic acids, furans and phenols (Lucian et al. 2018), its drying and/or storage might also change the concentration of these compounds. This may result in changes in its structure and surface chemistry, and consequently, in its behavior in

final applications (Benavente et al. 2022). For example, changes in organic compounds, including various aromatics, acids, and sugars, are crucial for understanding the chemical reactions (Tkachenko et al. 2022), and kinetic modeling (Reza et al. 2014) of HTC process and their potential impacts on applications like plant growth (Bargmann et al. 2013). Changes in inorganic elements such as heavy metals, phosphorus, and sulfur, can significantly influence the applicability of hydrochar in areas like agriculture and environmental remediation, and biofuel (Reza et al. 2013). Developing an understanding about the changes in physicochemical properties that can occur during storage and drying is crucial for choosing the best down-stream handling of hydrochar to achieve successful applications.

Therefore, this investigation was designed to determine whether the physicochemical characteristics of hydrochar change after production due to drying and/or storage conditions and which conditions can more effectively preserve the composition of hydrochar than others. Experiments were carried out to study the effect of storage temperature (20, 4 and -18 °C) on both wet and dry hydrochar by comparing the concentrations of organic and inorganic compounds over a one-year period to their control values measured directly after production. Statistical analysis was utilized to find the optimal storage conditions that result in the smallest changes in organic and inorganic compounds during storage. The results of this study will provide insights into the storage conditions that can preserve the composition of hydrochar, and will aid in the determination of appropriate storage conditions for future studies and applications in soil, environment, and fuel.

2 Materials and methods

2.1 Hydrothermal carbonization and storage experiments

The feedstock for the HTC process was digested cow manure obtained from a biogas plant operating at a cattle farm in Potsdam, Germany and stored at 4 °C until use. The elemental composition is found in Table 1; the slurry had a solid content (%So) of 19.0% wt, pH of 8.3, and a fiber distribution of 21.3% lignin, 19.0% cellulose, 2.3% hemicellulose, 37.4% rest organics, and 19.9% ash (Marzban et al. 2023). The experiment was conducted in a 18.75L reactor (Model 455, Parr Instrument, Moline, USA). The digestate as received was filled into the reactor (12.00 kg fresh mass (FM), %So=19.0%) and heated to 220 °C at a rate of 2 K min⁻¹ (temperature controller Model 4848BM, 6000-Watt 3 band heater) and held at a temperature of 220 °C for 3 h while being mixed at 200 rpm. This temperature was chosen for this study to achieve cellulose disintegration (Sevilla and Fuertes 2009), and attain a higher hydrochar yield compared

Table 1 The mean value and standard deviation of total solids (TS%), organic total solids (oTS%), Ash%, elemental composition (%) of feedstock and hydrochars served as control

Sample	TS%	oTS%	Ash%	pH	C%*	H%*	N%*	S%*	O%*	H/C*	O/C*
Feedstock	19.0	80.1±0.23	19.9±0.22	8.3±0.21	44.4±0.23	3.9±0.05	1.8±0.04	0.6±0.05	29.3±0.28	1.05±0.01	0.49±0.01
WH	30.8±0.26	82.9±0.23	17.1±0.10	7.7±0.10	56.5±0.62	3.1±0.07	3.4±0.07	0.7±0.04	18.9±0.63	0.65±0.01	0.25±0.01
DH	97.6±0.04	82.6±0.18	17.4±0.16	6.4±0.01							

*Dry basis (db)

to higher temperatures (Marzban et al. 2022). After the reaction, the reactor was cooled overnight, and the hydrochar was filtered through a vacuum filtration system (ROTH filter, pore size 5–8 μm). The filtered hydrochar was divided into two portions: one was left as wet hydrochar (WH), and the other was dried at 60 °C for 48 h (DH). The wet control sample was analyzed immediately after separation from the liquid and the dry control sample after the 48 h of drying. The remaining hydrochar was divided into 36 individual vacuumed plastic bags, with approximately 55 g in each bag, totaling 18 bags for the WH and 18 for the DH. These bags were divided into three groups to be stored at three different temperatures of 20, 4, and –18 °C and durations of 1, 2, 3, 4, 12, and 52 weeks. Vacuum sealing was chosen over unsealed bags to prevent microbial contamination, degradation and moisture variation. One bag of WH and DH was removed at the appropriate time for the analytical measurements. The storage experiment’s overall scheme is shown in Fig. 1.

2.2 Statistical analysis for storage recommendations

All analyses were conducted with at least triple repetition for each hydrochar sample (each bag), depending on the apparatus and technique used (details in Additional

file 1: Table S1). The results were reported as the mean and standard deviation. The statistical significance of the data was evaluated using ANOVA (Additional file 1: Tables S2–S5) and the storage recommendation was made based on Dunnett’s test to determine if the stored sample data was different from its control value (*p*-value less than 0.05). The analysis was carried out using JMP15 from SAS.

2.3 Analytical methods

The fresh and stored hydrochars were analyzed quantitatively and qualitatively over a one-year storage period using gravimetric and wet chemistry methods as well as elemental analysis, FTIR, SEM–EDX, XRD, HPLC, ICP–OES, total phosphorous and N–Kjeldahl. All chemicals utilized in this study were purchased from Carl ROTH, Germany. For some analyses, e.g., elemental analysis, ICP–OES, N–Kjeldahl and P total, samples were dried at 60 °C for 48 h and sample amounts were reported as gDM(60). For the HPLC analyses, the sample of wet or dry hydrochar was extracted as removed from the storage bags and the amount reported as g. To facilitate a comparison of the concentration of organic and inorganic compounds in wet and dry hydrochar, the measured concentrations were all converted into grams

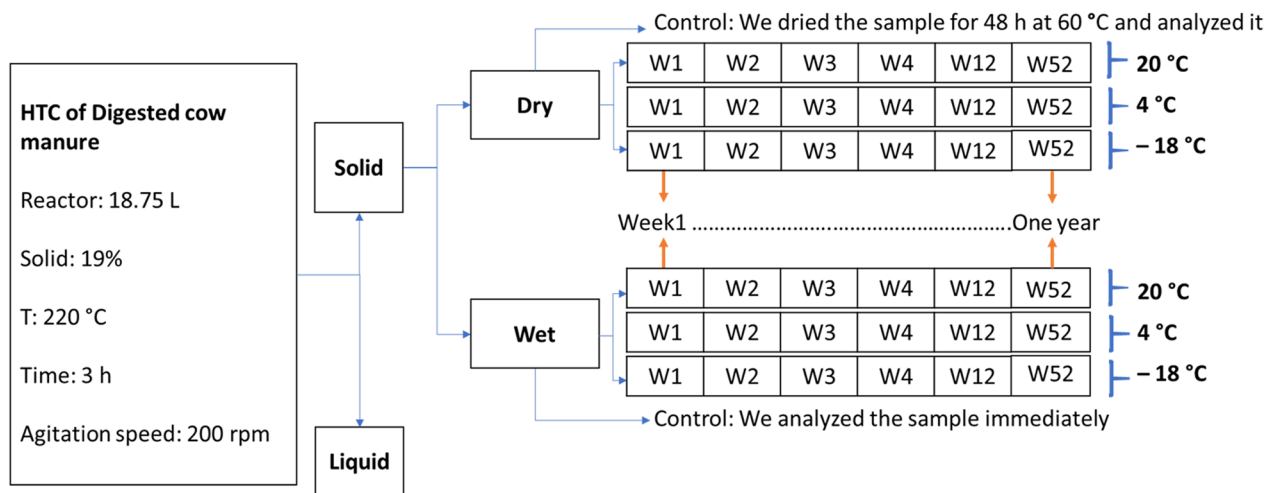


Fig. 1 Schematic of 1 year storage experiments of wet and dry hydrochar

per kilogram of dry matter (g kg^{-1} DM). The total solids (TS%) and ash content (ash%) in the feedstock and hydrochar were measured by drying at $105\text{ }^{\circ}\text{C}$ for 24 h, followed by $550\text{ }^{\circ}\text{C}$ for 5 h, according to DIN EN 14775. The organic total solids (oTS%) was calculated as the difference between TS% and ash%. The carbon, hydrogen, nitrogen, and sulfur elements were determined for 0.1 g DM(60) samples with the Elemental Analyzer Vario El (Elementar Analysensysteme, Hanau, Germany) with oxygen determined by difference.

To extract the hydroxymethylfurfural (HMF), catechol, fructose, glucose, sucrose, formic acid, lactic acid, and acetic acid from the hydrochar, 1 g of hydrochar (wet or dry) was mixed with 25 ml of distilled water at room temperature for 15 min at 150 rpm, and the resulting solution was then filtered using a PTFE syringe filter. The concentrations of sugars and acids were determined using the UltiMate 3000 UHPLC system (DIONEX-Thermo Fisher Scientific Inc., USA), using Eurokat H column and 0.01 N sulfuric acid as the mobile phase.

For the analysis of phenol, cresol, guaiacol, and furfural, 10 g of hydrochar (wet or dry) was weighed and mixed with 50 ml of distilled water and 5 ml of phosphoric acid, followed by steam distillation at $130\text{ }^{\circ}\text{C}$ for 7 min using the Vapodest 2000. The resulting liquid condensate was filtered using a PTFE syringe filter and measured using an HPLC system (Dionex ICS 3000; Thermo Fisher Scientific Inc., USA) equipped with a Eurospher C18 column. This HPLC system and filtration method were also used for the determination of HMF and catechol.

Here, the metals, phosphorus, and sulfur contents of the hydrochar were analyzed with an ICP-OES (ICAP6300 Duo, Thermo Fisher Scientific Inc., USA) equipped with an autosampler (ASX-520, CETAC Technologies, USA). A 0.1 gDM(60) ground sample of hydrochar was dissolved in 8 ml HNO_3 for 20 min in a microwave system, then centrifuged for 10 min at 4500 rpm. The resulting supernatant was analyzed with the ICP-OES. Total Kjeldahl nitrogen in hydrochar was determined following DIN EN 25663, in addition to the measurement of nitrogen content by elemental analysis. The ground sample (0.3–0.5 g DM(60) of hydrochar) was gradually heated with sulfuric acid to $400\text{ }^{\circ}\text{C}$ for digestion, converting nitrogen from proteins, urea, amides, amines, ammonium salts, etc. into ammonium sulfate. After steam distillation (Vapodest 30, Gerhardt, Germany), the ammonium sulfate was determined titrimetrically. Rapid digestion for phosphorous determination was carried out in conjunction with crude protein determination on the basis of Kjeldahl digestion. After this digestion of the sample, phosphorus was measured photometrically following the reaction with molybdate

vanadate in nitric acid solution containing ammonium according to DIN EN ISO 15681.

3 Results and discussion

3.1 Composition of control hydrochar samples

Comparison of the feedstock and hydrochar elemental composition after production showed that HTC increased the carbon content by 12.1%. The characteristics of the feedstock and control hydrochar samples are summarized in Table 1. The pH decreased from 8.3 in the feedstock to 7.4 in the process liquid and 7.7 for the wet hydrochar. Drying decreased the pH further to 6.4. This difference is likely due to the losses in organic acids due to drying as seen in Fig. 2a, and a decrease in cation release into water during sample preparation for pH measurement.

In general, the mass of the identified organic compounds was higher in the WH (15.2 g kg^{-1} DM) than in the DH (11.8 g kg^{-1} DM), and there were shifts in the concentrations of the organic groups and between the individual compounds (Fig. 2a, b). The content of total aromatics was decreased by 40% by drying (from 5.2 g kg^{-1} DM in WH to 3.1 g kg^{-1} DM in DH), while total sugars remained almost constant. The largest changes were seen in the individual organic acids, although as a group they only decreased by 16.2% (from 8.6 to 7.2 g kg^{-1} DM). After drying, the DH exhibited decreases in acetic and formic acid concentrations, but a fourfold increase in lactic acid. Some of the acetic acid may have evaporated during drying, and the decrease in formic acid may have been due to its conversion to CO_2 (Yu and Savage 1998; Marzban et al. 2023). To potentially prevent the loss of acetic acid and the reduction of formic acid to CO_2 , future studies could explore drying WH at temperatures below $60\text{ }^{\circ}\text{C}$ for more effective preservation of these acids. Wet hydrochar may contain substances that can transform into lactic acid during drying, for example, compounds derived from carbohydrates or other organic compounds in the biomass. These substances may undergo degradation under drying conditions, resulting in the release and conversion to lactic acid. Furthermore, Fig. 2a shows that DH has higher fructose and sucrose and lower glucose compared to WH, while the levels of HMF and furfural were slightly higher in DH. The increase in HMF could be due to further dehydration reactions of sugars (Sevilla and Fuertes 2009; Falco et al. 2011b; Parshetti et al. 2013) during the drying process at $60\text{ }^{\circ}\text{C}$ over 48 h, in which 96.5% of moisture in WH was removed. This can be also monitored by pH reduction from WH (7.7) to DH (6.4) after drying, in which slightly acidic condition may catalyze the conversion of sugars to HMF, the same typical reaction, which was observed during HTC process (Tkachenko et al. 2022). All the main

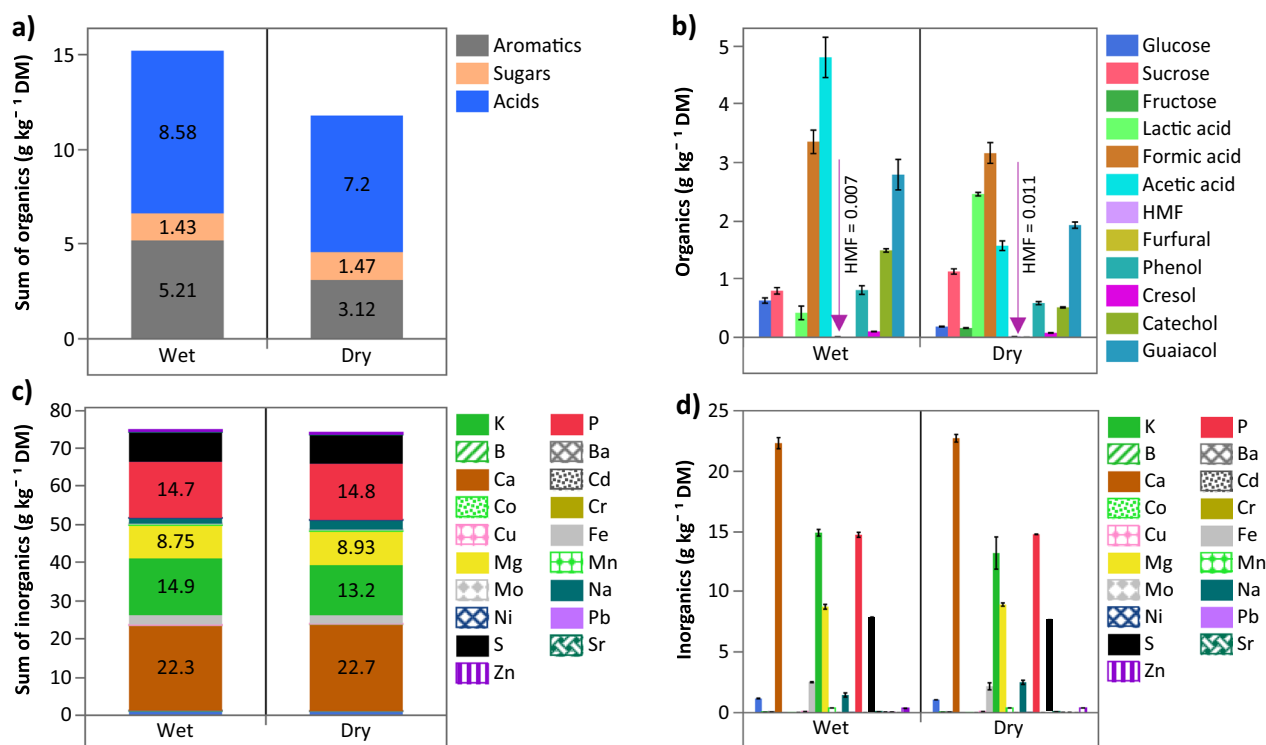


Fig. 2 The concentrations (g kg⁻¹ DM) in wet and dry hydrochar control samples for organics (sugars, aromatics and organic acids) as: **a** sum of organics, **b** individual compounds with standard deviation, and for inorganics measured by ICP-OES as: **c** sum of inorganics, **d** individual compounds with standard deviation

HTC products of dissolved lignin (phenol, catechol, guaiacol, and cresol), which can polymerize to form secondary phenolic char under HTC conditions (Fang et al. 2008; Kang et al. 2012) were present in the control WH and DH samples, though their concentrations were lower in DH compared to WH. This variation could be attributed to the hydrochar matrix during the drying process, which likely facilitated stabilization and consequently resulted in decreased extraction. The significant decrease in catechol (66%) could be due to its oxidation during drying (Wojdyło et al. 2014; Kieu Tran et al. 2020). No statistically significant difference was observed between the inorganic elements detected by ICP-OES method in the control wet (WH) and dried hydrochar (DH). The majority of the inorganic elements (Fig. 2c, and d) showed little variation after the drying process.

These observations are backed up by the results of the mass balance on the WH considering the concentrations of the compounds in the process liquid remaining in the fresh char. Even after vacuum filtration, approximately 70% of the WH sample was water. Using the process liquid concentrations as detailed in our previous study (Marzban et al. 2023), a comparison was made between the mass of the compounds contained in the process liquid associated with the WH to that which was extracted

from the WH by the analysis methods (see Additional file 1: Table S6). For most of the aromatics (except cresol), and two of the three sugars (glucose and sucrose), there is more compound mass found in the WH than that attributing to the process liquid; therefore, the compound was not present just due to the process liquid held in the char, but also contained in the char itself. In contrast, for the three organic acids, cresol and fructose, there is less mass in the hydrochar than expected from the process liquid. This indicates that these particular compounds are introduced into the wet hydrochar from the process liquid, and were either partially lost during sample preparation or not extracted by the current methods.

3.2 Changes in lumped parameters over storage time

The measurement of pH over the storage time showed that the difference between the WH and DH remained, and the values did not change greatly over the year (Fig. 3a). WHs and DHs stored at -18 °C showed the least change in pH. A slight initial increase in the pH of WHs may be due to the desorption of cations into the surrounding moisture, but this only occurred in the first week. The TS% of DHs remained unchanged when stored at -18 °C until week 12, while reductions were observed after 2, 4, and 12 weeks at 4 and 20 °C (Fig. 3b).

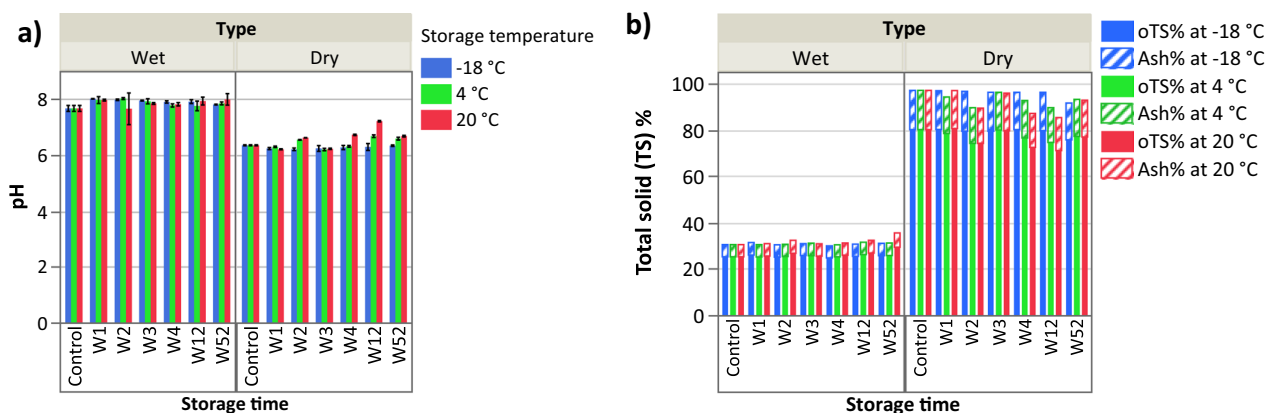


Fig. 3 The changes of **a** pH and **b** total solids (TS%) including the ash% and organic total solids (oTS%) in DH and WH at different storage temperature over the storage time

There are a few possible reasons for these changes. First, the organic compounds may volatilize during the heating up to 105 °C for TS% determination, causing a decrease in TS% in stored samples at 4 and 20 °C for 2, 4, and 12 weeks (Fig. 3b), which has a good agreement with oTS% reduction at these conditions. Second, this decrease might be related to the moisture redistribution in the sample, causing a heterogeneity in the sample, thus decreasing the TS% while increasing the pH. In contrast, WHs and DHs stored at -18 °C showed more stable pH and TS% values compared to other temperatures. The results showed that higher storage temperatures for DH resulted in greater changes in pH, TS, and oTS%. These changes are likely attributed to heterogeneous moisture redistribution within the sample.

The results of the elemental analysis over 1 year storage show the lowest changes in C, H, N and S for DH stored at -18 °C, while those stored at 4 and 20 °C showed

significant changes, especially after week 4 (Fig. 4a). The stored WH at week 52 showed the same changes as DH. Changes in elemental composition were followed only for the DH periodically over the storage time.

To gain an indication about possible changes to the degree of oxidation of the compounds and/or heating values, the Van Krevelen diagram comparing the control and stored hydrochars is shown in Fig. 4b. As can be seen, the O/C ratio of the sample stored at -18 °C remained almost constant. However, the WH and DH samples stored for 52 weeks at 4 and 20 °C displayed an elevated O/C ratio. This change can be attributed to a decline in the carbon content (C%) and/or a rise in the oxygen content (O%). These findings indicate the possibility of hydrochar oxidation taking place either during the storage period or during the sample preparation process for elemental analysis. The instability of phenols due to autoxidation during storage may be one reason.

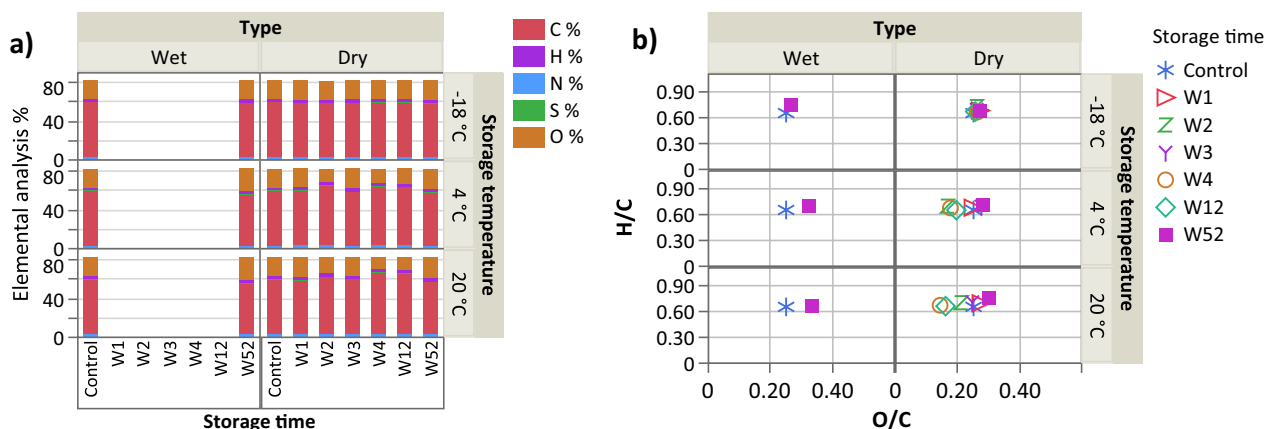


Fig. 4 **a** Changes in elemental composition (C, H, N, S, and O%), and **b** Van Krevelen diagram of wet and dry hydrochar over 1 year of storage at different temperatures (changes in elemental composition were followed only for the DH periodically over the storage time)

In contrast, the O/C ratio of the DH samples stored at 4 and 20 °C for 4 and 12 weeks decreased, which may be attributed to an increase in C content likely caused by: (1) chemical reactions or loss of compounds (e.g., methanol or formic acid) and (2) heterogeneous moisture redistribution within the DH samples. The increase in C content may contribute to an improvement in the higher heating value (HHV) of the DH samples (Marzban et al. 2022).

The change in nitrogen content was followed by both elemental analysis and N-Kjeldahl. After a year of storage, a similar difference in N content between the dry and wet samples remained at all storage temperatures, for DH ranging from 28.5 (control) to 30.5, 30.7, and 30.1 (g kg⁻¹ DM) for -18, 4, and 20 °C, respectively, and for WH from 32.9 (control) to 34.3, 34.4, and 34.0 (g kg⁻¹ DM) for the respective temperatures. Analysis of the N-Kjeldahl content of WH and DH controls showed a 13% reduction in the DH sample compared to the WH (Additional file 1: Fig. S1). The observed decrease in N-Kjeldahl may potentially be attributed to the volatilization of nitrogen-containing compounds, such as ammonia, during drying. For the N-Kjeldahl sample preparation, the wet hydrochar (WH) was dried, and the dried hydrochar (DH) was further re-dried at 60 °C. The changes also were observed for N measured in DH (stored for 4 and 12 weeks) using elemental analysis. To prevent potential alterations, we proposed using an alternative method for sample preparation, such as lower drying temperatures (freeze-drying) of WH, especially for hydrochar produced from feedstocks with high nitrogen content, like digestate. This approach may minimize changes during sample preparation for analysis.

3.3 Changes in organic compounds over storage time

The concentrations of the organic compounds changed significantly over the one year storage time. Figure 5a–c depict these changes during storage for each of the groups: sugars, acids, and aromatics (figures for each individual compound are found in the Additional file 1: Fig. S2). The composition and concentrations of the sugars differed between the DH and WH control samples and this difference became significantly larger in the storage samples, especially at week 52. For glucose, both DH and WH initially showed a slight decrease in content for the first 12 weeks. However, glucose content increased significantly from week 12 to 52, regardless of wet or dry or storage temperature, with the highest content in WH samples stored at -18 °C. For sucrose, the wet samples showed a similar decrease-increase pattern, with a significant increase from weeks 12 to 52, while in DH it remained at a higher level. In contrast, fructose increased at week 52 of storage in DH stored at temperatures of

4 °C < 20 °C < -18 °C, while no fructose was found in WH samples.

The increase in sucrose and glucose content of WH may be due to further degradation of unreacted biomass in the HTC solid product. This is supported by the detection of residual biomass particles in the final hydrochar product through SEM–EDX and XRD analysis, discussed in the following section. We suspected that a long exposure (1 year) of WH with a high moisture content (69%) and a relatively high pH (7.7) may promote hydrolysis into sugars. For example, alkaline pretreatment of biomass has been reported as an efficient technique for yielding sugars (Loow et al. 2016). Additionally, the weakening and breaking of bonds in the matrix of stored WH and DH could also lead to the release of these compounds during sample preparation.

These increasing trends over the year with higher amount for WH were seen for most all groups of the organic compounds. The formic acid content remained stable for 12 weeks of storage, but significantly increased from week 12 to 52 for DH stored at -18 °C, and WH stored at -18 °C and 4 °C. Lactic acid was higher in DH than WH at most temperatures and times, and significantly increased from week 12 to 52 for WH, with the highest amount found for samples stored at 20 °C. The lactic acid in dry samples (-18 °C and 20 °C) increased from week 3 to week 52, but for 4 °C, it increased only up to week 12 and then decreased. Acetic acid was higher in wet samples at all storage times and temperatures, and remained constant until week 12 for both WH and DH, after which it significantly increased. The increase in acids during storage may be related to the increase in sugars, as they are formed by the hydrolysis of cellulose (Kruse et al. 2013) and hemicellulose (Jing and Lü 2007) during HTC conditions.

The phenolic compounds (phenol, guaiacol, and cresol) also increased significantly after 52 weeks of storage compared to control, with higher content found in WH. Catechol followed the same trend as the other phenols in WH but decreased slightly in DH at all storage temperatures over time, instead of peaking at week 52. Such instability in phenolic content is a known phenomenon during the processing and drying of food products (Cao et al. 2021). For example, the autoxidation's potential to cause a decline in polyphenol content occurs following the process of oxidative polymerization and degradation. The rate of these reactions is influenced by factors such as temperature, pH, and the partial pressure of oxygen (Sang et al. 2005). In general, the WH has more aromatics than DH. For example, from week 4 to 52, guaiacol increased 130% (from 3.01 to 6.96 g kg⁻¹ DM) in WH stored at -18 °C, 137% (from 2.93 to 6.95 g kg⁻¹ DM) in WH stored at 4 °C, and 47% (2.82 to 5.3 g kg⁻¹

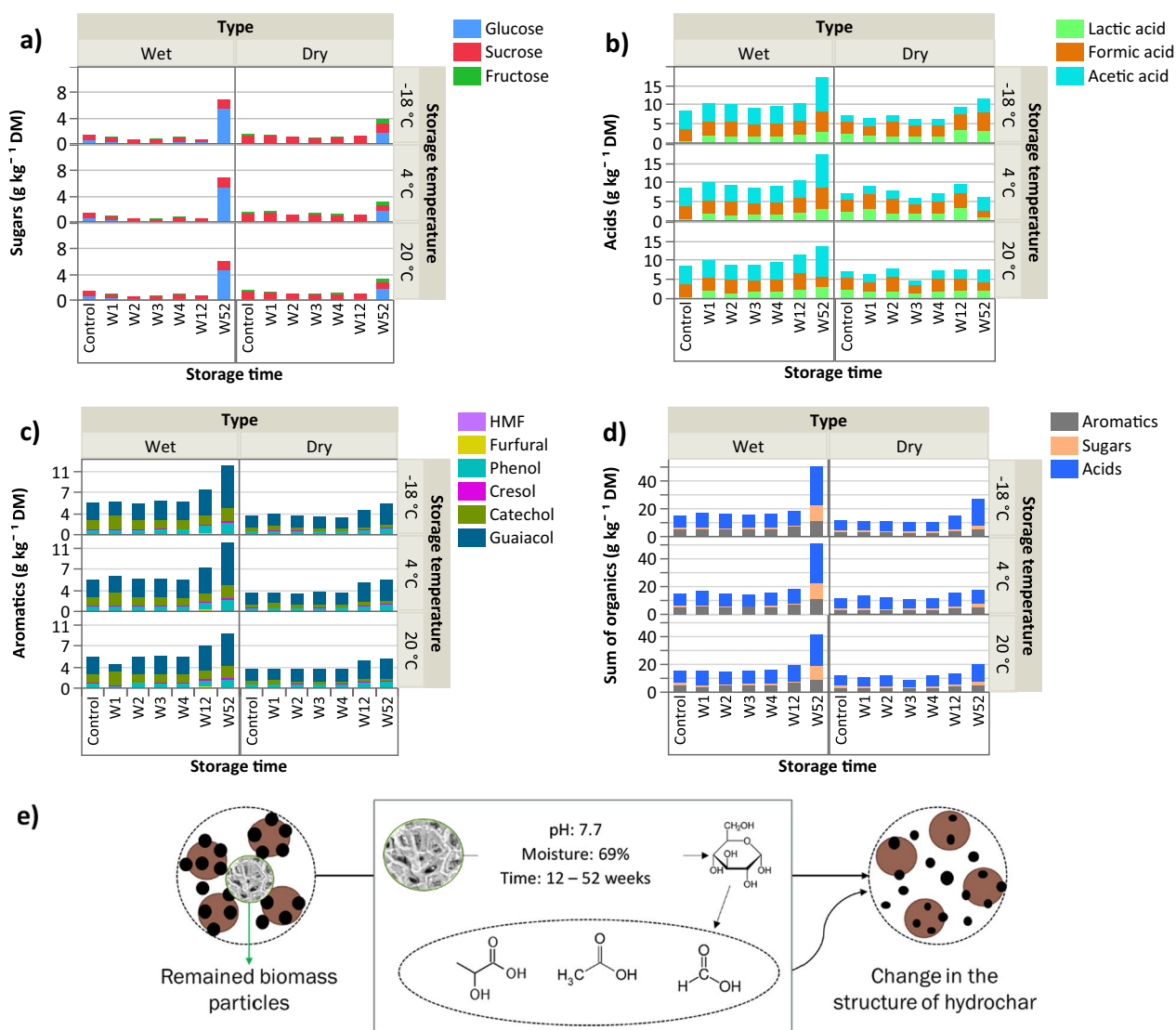


Fig. 5 Changes in **a** sugars, **b** acids, **c** aromatics of wet and dry hydrochars at different temperatures while in storage, **d** sum of organics, and **e** illustration of possible changes in wet hydrochar. (Individual figures for each organic compound as well as Dunnett's test for sum of organics can be found in Additional file 1: Fig. S2 and Table S7)

DM) in WH stored at 20 °C. In DH, guaiacol increased 89% (from 1.82 to 3.44 g kg⁻¹ DM), 84% (from 1.9 to 3.5 g kg⁻¹ DM), and 67% (from 2.01 to 3.36 g kg⁻¹ DM) for storage at -18, 4, and 20 °C, respectively. The results showed that the guaiacol increased more at lower storage temperatures (-18 and 4 °C) than 20 °C. Both HMF and furfural reached their highest levels at week 12 for both wet (WH) and dry (DH) samples, with an approximate 12-fold increase for HMF (from 0.01 to 0.12) and a 20-fold increase for furfural (from 0 to 0.2) in the wet sample. In the dry sample, HMF demonstrated a four-fold increase (from 0.01 to 0.04), and furfural exhibited a ninefold increase (from 0 to 0.09), all compared to the

respective control values. After 1 year, however, their concentrations decreased somewhat.

Figure 5d illustrates the total concentration of identified organic compounds, such as sugars, aromatics, and organic acids, throughout a one-year storage period at various temperatures. The findings reveal notable variations in these compounds, particularly an evident increase at week 52 when compared to the control values. Aromatics demonstrated a significant rise of 80–120% in the case of WH, and 58–68% in DH, relative to the control. Notably, this increase was more pronounced when the storage temperature was lower than 20 °C for both WH and DH. Furthermore, the total sugar content

exhibited a substantial increase. To illustrate, there was an approximate sevenfold rise in WH, while DH exhibited a comparatively lower increase of around twofold. Remarkably, the most substantial increase was observed in samples stored at $-18\text{ }^{\circ}\text{C}$ for both WH and DH. In addition to sugars and aromatics, the total organic acid content experienced a considerable increase in comparison to the control. WH showed a higher elevation of 156–371%, whereas DH demonstrated an increase of 36–159%.

3.4 Changes in inorganic compounds over storage time

The variation in the content of most inorganic elements over 52 weeks of storage (Fig. 6), was much less than that seen for the organic compounds, the differences ranging between 0%–30% when compared to the control values, except for Ni, Mo, Tl and Ti (up to 100% different). The ANOVA analysis to determine the effect of the storage time and temperature on the measurement of the 24 inorganic elements showed that DH was significantly more stable than WH over the 52 weeks (Additional file 1: Tables S4 and S5). While 11 elements in the DH showed a statistically significant change from the time of control sample until the week 52 ($p\text{-value} \leq 0.05$), the content of all 24 elements measured by ICP-OES changed in WH.

The Dunnett test, which detects when the content differed significantly from the control, supported the

conclusion from the ANOVA test: measurement of char stored under dry conditions produced values more consistent with the control values except for Pb and Ti (Table S9). For 16 of the 24 elements, the DH can be stored over the whole 52 weeks at $20\text{ }^{\circ}\text{C}$ or $-18\text{ }^{\circ}\text{C}$ with no significant change. Of the nine heavy metals regulated in either soil amendment or fuel standards (Cu, Cr, Cd, Ni, Pb, Zn, V, Tl, and Mo), four showed some increases in content after the 52 week storage time (Cd, Co, Tl, and Zn), while two showed no significant changes (Cr and Cd) and three decreased (Mo, Ni, and Pb). In the WH, there were 7 elements which did not present any statistically significant change when stored at $20\text{ }^{\circ}\text{C}$ (which was the best storage temperature for the WH). These elements included Cr, Cu, Mn, Pb, Sr, Ti and W. Therefore, it is recommended to store the DH at $20\text{ }^{\circ}\text{C}$ for inorganic analysis for measurement before week 12. If Pb and/or Tl have to be measured, they should be analyzed up to storage week 4.

These unexpected changes in the content of inorganic trace elements in the hydrochar may be due to analytical difficulties or element instability. A review of the results from numerous international interlaboratory comparisons of trace elements in a variety of organic matrices has shown differences in content between 1 to 5 orders of magnitudes (Dybczyński 2019). The analytical challenges stem from multiple factors, including

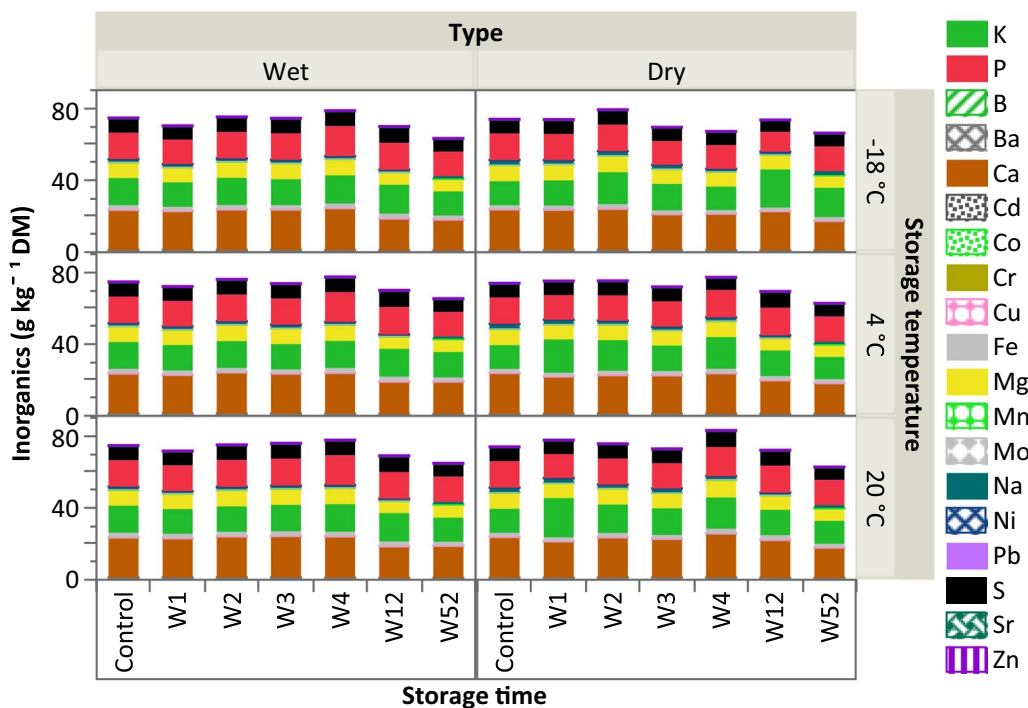


Fig. 6 Changes in inorganics measured by ICP-OES method for wet and dry hydrochar at different temperatures over storage time (individual figures for each inorganic as well as Dunnett’s test for sum of inorganics can be found in Additional file 1: Fig. S3, and Table S8 respectively)

sample inhomogeneity, analyte loss through processes like volatilization, adsorption, and incomplete dissolution, as well as the potential addition of trace elements from laboratory materials and reactions with the sample constituents (Dybczyński 2019). Furthermore, the instability of inorganic elements, which may undergo precipitation formation or redox reactions during storage and processing, further challenges the accurate quantification of these elements, particularly at low content in the mg kg^{-1} or $\mu\text{g kg}^{-1}$ range. Although the hydrothermal carbonization process used to produce the hydrochar may enhance the stability of some inorganic compounds, it does not eliminate their reactivity entirely. Previous studies have revealed that a considerable fraction of certain metals remains soluble, oxidizable, or reducible even after hydrothermal carbonization, indicating ongoing reactions and changes in mobility over time (Huang and Tang 2015; Zhai et al. 2016; Huang et al. 2018a; Lang et al. 2019). For example, Huang et al. (2018b) found that 90% of the Zn in the hydrochars produced at 225 °C from sewage sludge was unstable: 10% was soluble, 20% was reducible and 60% was oxidizable (Huang et al. 2018b). In a similar study, it was found that up to 45% of the P in hydrochar from swine manure was water soluble. Furthermore, the study from Zhai et al. (2016), demonstrated that up to 70% of the share of Cu, Pb and Zn can be either solubilized, oxidized, or reduced (Zhai et al. 2016). These complexities highlight the need for future research and careful consideration when interpreting and analyzing inorganic trace elements in hydrochar samples. Furthermore, the speciation of inorganics, such as water-soluble and acid-soluble forms, necessitates additional studies to understand how these characteristics may change during storage.

These aspects are especially relevant for judging compliance with the different regulations and voluntary standards that set limit values for the content of inorganics in various hydrochar applications, such as the European Biochar Certificate (EBC) for agricultural use. All but two elements measured in this study and regulated by the EBC fulfilled the limit values for all storage conditions: Cu and Zn. In the case of copper, the measured values were consistently around the upper limit for the AgroClass ($100 \text{ mg kg}^{-1} \text{ DM}$) for all samples. In contrast, while the content of Zn in the control samples was slightly below the limit value ($400 \text{ mg kg}^{-1} \text{ DM}$) at 374 and 388 $\text{mg kg}^{-1} \text{ DM}$ for WH and DH, respectively, after the third week of storage, the mean value in the WH exceeded the limit at all storage temperatures and the DH only at 20 °C. The choice of storage conditions makes no difference for Cu, but can affect the meeting of Zn limit values.

3.5 Characterization of hydrochars over storage time

The surface structures and composition of feedstock and hydrochars were characterized using SEM–EDX, XRD and FTIR analyses. Figure 7a and b show the remaining plant cell walls in the digestate and the control hydrochar identified by SEM–EDX. These non-reacted components of biomass were retained within the hydrochar particles and their breakdown through storage and handling may contribute to the variations seen in the contents of sugars and organic acids over the storage time. The EDX results (single point, highlighted red) indicate an enrichment of carbon content and a reduction in oxygen content after HTC. However, the SEM–EDX analysis of WH and DH samples stored at –18, 4, and 20 °C (Additional file 1: Fig. S4) did not show any visible changes.

The presence of unreacted cellulose after the hydrothermal treatment is seen in the XRD analysis of hydrochars as two broad maxima centered at ca. 2θ 18 and 26 (Fig. 7c and d). The inorganic components of the hydrochar such as SiO_2 , KCl, $\text{CaMg}(\text{CO}_3)_2$ and CaO were also identified in the XRD signals. The presence of these mineral phases is in a good agreement with the EDX elemental analysis of the samples. Additionally, the FTIR spectra of all samples exhibited typical features of the hydrochar, and only slightly change during the storage (Fig. 7e and f). Notably, dry samples had a lower intensity of the broad band at $3700\text{--}3000 \text{ cm}^{-1}$ that corresponded to the overlapped vibrational modes of the O–H bond on the carbon surface and the adsorbed water. Distinct band at 3270 cm^{-1} corresponding to the stretching of N–H and deformational N–H vibrational mode at 1595 cm^{-1} revealed the presence of primary amino functionalities in the hydrochar. Two bands at 2924 and 2850 cm^{-1} corresponded to asymmetric C–H vibrations and, together with bands at 1450 and 1430 cm^{-1} point to the presence of the aliphatic functionalities. The band at 1512 cm^{-1} corresponded to C=C vibration in aromatic homocyclic compounds. The bands in the range $1158\text{--}1016 \text{ cm}^{-1}$ corresponding to the C–O vibrations of the pyranose form of saccharides were characteristic for the cellulose. This is supported by the XRD data of the samples. The FTIR spectra of WH and DH during weeks 1–12 of storage are presented in Additional file 1: Fig. S5.

3.6 Recommended storage condition

In this section, the storage recommendations for analyzing hydrochar in future HTC studies and for use in various applications were discussed. Knowledge about the stability of specific organic compounds, including various aromatics, acids, and sugars, will help improve studies on the kinetic modeling of the HTC process and its chemical reactions, as well as the experimental design for applications using hydrochar, such as determining the impact

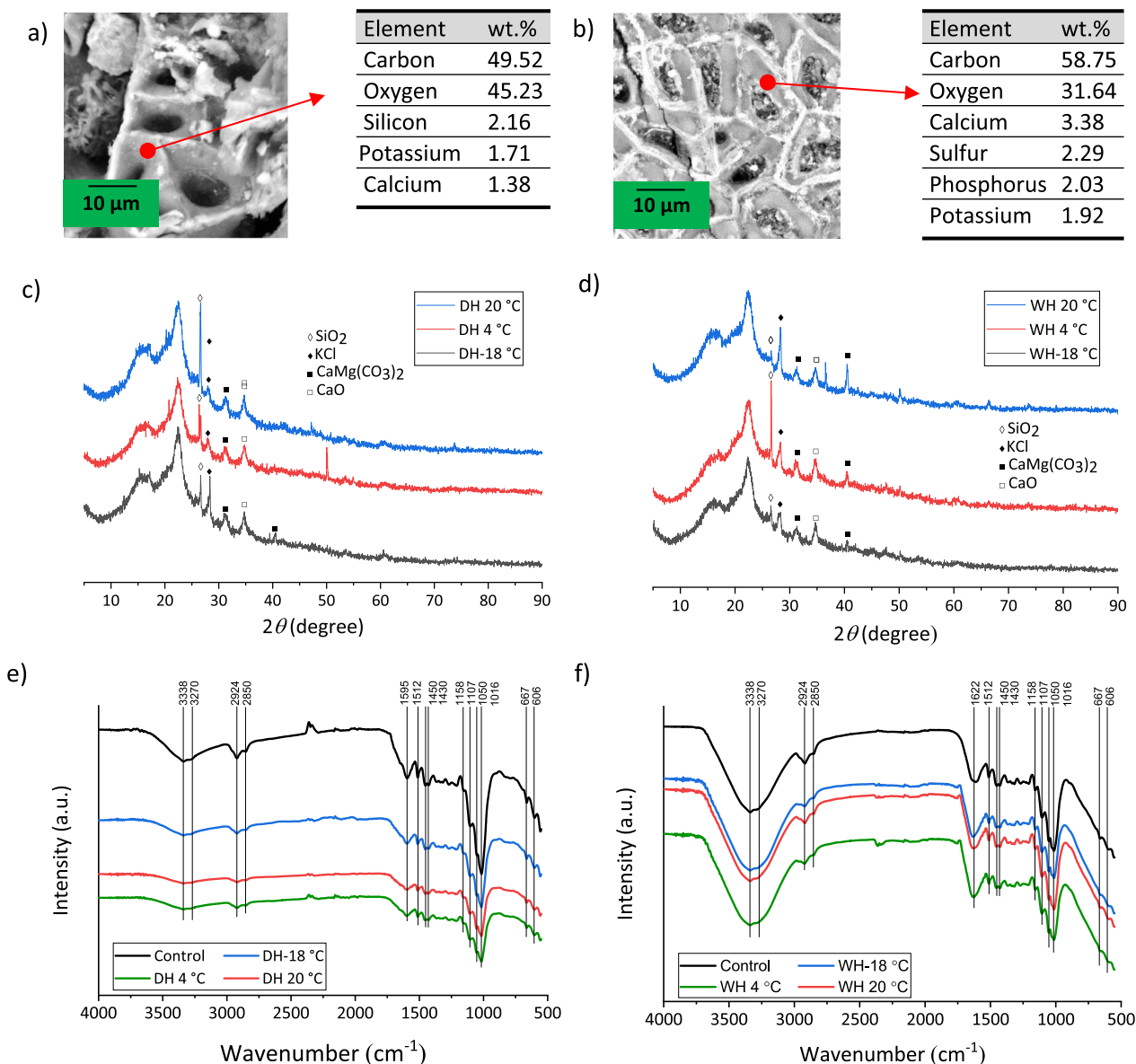


Fig. 7 SEM and EDX (single point) analysis of **a** digestate cow manure, and **b** control hydrochar; XRD of **c** DH, and **d** WH after 52 weeks of storage; FTIR spectra of controls and **e** DHs, and **f** WHs stored for 52 weeks compared to the control (FTIR spectra of week 1 to 12 can be found in Additional file 1: Fig. S5a and b)

of hydrochar on plant growth. Potential changes in inorganic elements such as heavy metals, phosphorus, and sulfur can play a role in determining whether hydrochar meets limit values in regulations for agricultural, environmental and biofuel applications. Firstly, storage recommendations were presented, based on the statistical evaluation of the results, to guide the approach to HTC studies, which normally have the goal of identifying the compounds present in the hydrochar directly after production. Then, the discussion shifts towards the possible applications for the stored hydrochar, considering the

potential changes that can be expected from storage of the hydrochar and how these changes can be exploited to reach the application goals.

3.6.1 For HTC studies

The results of the ANOVA analysis (Additional file 1: Tables S2 and S4) show that the time of storage has a significant impact on the changes of both organic and inorganic compounds in WH and DH. Therefore, the timing of analysis is crucial in determining

Table 2 Summary of recommended storage conditions for the DH and WH of this study and for HTC process liquid outlined in our earlier study (Marzban et al. 2023)

		Liquid (Marzban et al. 2023)			Wet hydrochar			Dry hydrochar		
		-18 °C	4 °C	20 °C	-18 °C	4 °C	20 °C	-18 °C	4 °C	20 °C
Aromatics	HMF	W3	W3	W3	0	0	0	W1	W1	0
	Furfural	NA	NA	NA	W4	W4	W4	W1	W2	W4
	Phenol	0	0	0	W12	W4	W4	0	W4	W12
	Catechol	W1	W1	W1	W4	W4	W4	0	0	0
	Guaiacol	W2	0	0	W4	W4	W4	W4	W4	W4
	Cresol	W4	W4	W4	W4	0	0	W2	W4	W4
Organic acids	Acetic acid	W12	W3	W12	W12	W1	W12	W12	0	0
	Lactic acid	0	0	0	0	0	0	W12	W4	0
	Formic acid	0	0	0	W1	W12	W4	W12	nsc	W2
Sugars	Glucose	0	0	0	0	0	0	0	W2	0
	Sucrose	0	0	0	W1	0	W1	W2	W4	W1
	Fructose	NA	NA	NA	0	0	0	W1	W1	0
N		NA	NA	NA	NA	NA	NA	nsc	W1	W1
C		NA	NA	NA	NA	NA	NA	nsc	nsc	W1
H		NA	NA	NA	NA	NA	NA	nsc	nsc	W1
Ash%		NA	NA	NA	nsc	W12	nsc	nsc	0	0

The color and coding (0 to nsc) represent the maximum duration for storing samples before observing the first significant changes compared to their control values. Dark green: no statistically significant changes (nsc) occurred compared to the mean control over 52 weeks of storage, light green: no change in the 12th week; yellow: no change in the 4th week; light orange: no change in the 3rd week; dark orange: no changes after 2nd week; light red: no changes in 1st week of storage; dark red: no storage is recommended; NA means the data was not available to make the decision for storage, nsc means no significant

the properties of hydrochar. To avoid misreporting in future studies, we proposed recommended storage conditions to minimize changes from the control values (Table 2). For example, storing DH samples at 4 °C for 2 to 4 weeks showed no significant changes in glucose and sucrose content compared to control values. However, in WH, the glucose content changed significantly during storage and no storage is recommended. WH sucrose content showed no significant changes after one week of storage at -18 °C and 20 °C. For aromatics like HMF and phenol, guaiacol, cresol, we suggested storing DH at -18 °C for 12 weeks and WH at 4 °C for 1 week and -18 °C for 4 weeks, respectively. For organic acids, formic acid can be stored at -18 °C for 12 weeks in DH, while lactic acid should be analyzed before storage and acetic acid can be analyzed up to 12 weeks of storage at -18 °C and 4 °C for WH, respectively. The recommended storage conditions for the elemental analysis, ash%, TS%, oTS%, and pH of DH are at -18 °C. However, maximum storage times may vary. For inorganics measured by ICP-OES, N-Kjeldahl and P total, the storage recommendations are summarized in Additional file 1: Table S9. The table also includes the recommended storage condition reported in our previous work (Marzban et al. 2023), showed the individual aromatics -18 °C from 1 to 4 weeks, while acetic acid can be stored at -18 and 20 °C for 12 weeks. However,

no storage was recommended for lactic, formic acids, glucose, and sucrose.

3.6.2 Storage recommendation for applications

Often hydrochar must be stored before application for a number of reasons, e.g. in order to produce sufficient quantities, waiting for transportation or further processing. In this section, we explored if the type of post-treatment and length of storage can be varied to optimize char characteristics specifically for the planned application as a soil amendment or as a biofuel.

Hydrochar has been shown to possess the potential for enhancing soil humic substances by providing substrate for microbial and fungal communities (Sun et al. 2020). However, the extent of this effect is influenced by factors such as pH and the release of organic compounds, including sugars, amino acids, and phenols (Yang and Antonietti 2020). The humic substances enhance the germination index (Ghaslani et al. 2024), and aid plants in uptaking more nutrients (Ghaslani et al. 2024; Volikov et al. 2024). In particular, WH exhibits a higher pH and can release a greater quantity of organic compounds, potentially promoting the process of humification in the soil. This must be weighed against possible inhibition of microbial populations by high levels of phenolic compounds (Souto et al. 2000) and the desired microbiome composition. For example, studies have reported that fungi were more abundant at acidic and slightly

acidic pH, while increasing the pH from acidic to neutral resulted in bacterial richness (Sun et al. 2020). The release of nutrients from hydrochar in the soil depends on soil type and hydrochar to soil ratios (Bento et al. 2019). However, a higher pH and nutrient concentration may negatively affect seed germination (Pérez-Fernández et al. 2006). Additionally, the presence of phenolic compounds or acetic acid has been observed to decrease both seed germination rate and root length (Busch et al. 2013; Bargmann et al. 2013; Kern et al. 2017). Treating hydrochar post-production, specifically through methods like water washing, has been reported as an effective method to increase the grain yield (Wu et al. 2021). Recent study reported that fresh hydrochar negatively affects tomato seed growth, while post-treated hydrochar (washed and thermally treated) enhances germination by 10–20% in marginal agricultural soil at low dosages (Suarez et al. 2023). They observed less toxicity in washed hydrochar since washing removes most organic acids, volatile fatty acids (VFA) and toxic compounds, leaving low levels of phenolic compounds (Suarez et al. 2023). Therefore, for seed germination and plant growth, it is recommended to use DH stored for no longer than four weeks, since prolonged storage may cause considerable release of aromatics and organic acids. Additional post-treatments like washing may be necessary before application. It is essential to conduct further studies to comprehend the effects of using both fresh and stored hydrochar in the applications mentioned above.

In order to minimize ammonia emissions from the soil, soil application of acidic hydrochar has been found effective (Maniscalco et al. 2020). Therefore, as DH had a lower pH than WH, dry hydrochar may be more beneficial. Future studies should investigate the changes in hydrochar over time, in both presence and the absence of soil. The application of hydrochar for heavy metal removal from soil showed better heavy metal immobilization for hydrochar with higher pH values (Xia et al. 2019), in our case WH, while hydrochar with lower pH, here DH, and presence of Al, Ca, Fe and Mg ions can

reduce phosphate content (Maniscalco et al. 2020). To effectively adsorb pollutants from the aqueous phase, we recommend using DH (either fresh or, if storage is required, DH stored for no more than 4 weeks). DH maintains its characteristics better (compared to WH) and minimizes the release of organic and inorganic compounds, which can be considered water pollutants. Nevertheless, a post-treatment step, such as thorough washing, may be necessary before application to ensure the removal of water-extractable organic and inorganic compounds. The employment of washed and unwashed hydrochar for the adsorption of particular pollutants from water, while tracking its organic and inorganic release (desorption), requires additional research.

Another application of hydrochar is its use as a biofuel. Storage had little or no effect on the relevant biofuel properties (e.g. C and O content) over the year (for both WH and DH) and therefore no special recommendations are necessary. In the context of biofuel applications where hydrochar may need to be pelletized, storing the dry DH in pellet form can facilitate transportation and application. Further studies are necessary to determine how the process of pelletizing influences the characteristics of hydrochar during storage.

Considering these insights for different applications, it is important to note that storing hydrochar at constant temperature, specifically at low temperatures (−18 °C, 4 °C) for extended periods may not be feasible due to high energy demands. This is particularly relevant as Table 3 summarizes the hydrochar type and time of storage based on the aforementioned discussion. Future research might explore room temperature storage, both in sealed and unsealed conditions. However, under these conditions, it is important to assess microbial impacts, potential gas emissions, and how moisture content variations in unsealed conditions could affect hydrochar properties. These conditions require further investigation, focusing on storage costs and energy requirements compared to constant storage

Table 3 Suggested type and storage time for different potential applications of hydrochar

Application	Goal	Suggested hydrochar	Storage condition
Soil amendment and agriculture	Increase the soil humic substances	Wet	Up to 1 year
	Microorganisms	Dry	Up to 4 weeks
	Germination and plant growth	Dry	Up to 4 weeks
Soil remediation	Immobilization of heavy metals	Wet	Up to 12 weeks
	Reduce phosphate	Dry	Up to 12 weeks
Water purification	Adsorption	Dry	Up to 12 weeks
Biofuel		Dry or Wet	Up to 1 year

temperatures, and should include life cycle assessment as well as cost and energy analysis of hydrochar storage.

4 Conclusions

In this study, we investigated the impact of moisture, storage time and temperature on hydrochar produced through hydrothermal carbonization from digestate from cow manure. Drying hydrochar resulted in large changes in organic compounds, decreasing the content of the five selected aromatics by 40% and three organic acids by 16.2%, improving its suitability for soil applications, while inorganic compounds remained relatively unaffected. During storage, organic compounds, including phenols, sugars, and acids, increased in both dry and wet hydrochar compared to controls, regardless of storage temperature. Statistical analysis showed the time of storage and moisture have a significant effect on hydrochar stability. Catechol was particularly sensitive to storage and its content should be measured immediately after the synthesis. WH showed significant changes also in lactic acid and glucose content, making storage not recommended. Considering the changes, which might happen after drying of fresh hydrochar, for future studies with the goal of measuring after-production conditions, if storage is needed, DH samples should be stored at $-18\text{ }^{\circ}\text{C}$ or $4\text{ }^{\circ}\text{C}$. DH generally showed greater stability over time, suggesting its suitability for a range of applications where stability is key. Conducting an analysis before usage is crucial to ensure that the hydrochar retains its desired properties for effective and reliable use. Moreover, it is important to carefully investigate the use of fresh and stored hydrochar for potential applications suggested in this study.

This study underscores the need for further research into hydrochar storage, particularly due to the unexpected change in the measured inorganic concentrations during storage, which necessitates careful consideration. The speciation of inorganics, such as water-soluble and acid-soluble forms, requires further investigation to understand how these characteristics might change during storage. While this study focused on hydrochar produced from cow manure digestate at $220\text{ }^{\circ}\text{C}$, it is crucial to understand how processing conditions affect hydrochar stability. Future research should examine whether hydrochars from various feedstocks, like lignocellulosic biomasses, undergo similar physiochemical changes during storage. Long-term storage at constant temperatures may not be practical or economical due to high energy requirements. Therefore, exploring alternative storage methods, including the use of sealed or unsealed bags at uncontrolled temperatures, is important, taking into account potential impacts from microbial activity and moisture. Investigating the effects of drying hydrochar at different temperatures and monitoring the chemical

changes during this process is essential, particularly to understand the potential changes in organic compounds, such as sugars and acids. Evaluating the environmental and economic impacts of post-treatments, like drying and washing, is crucial for balancing the benefits against the costs and determining the necessary compromises for various application goals. Additionally, in the area of long-term carbon storage, conducting comparative studies between storing hydrochar in soil versus containers could present an interesting area for future research.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1007/s42773-024-00329-y>.

Additional file 1: Table S1. Replications of measurement for separate samples performed for statistical data analysis. **Table S2.** Results of the one way ANOVA for aromatics, sugars, organic acids, TS%, oTS%, Ash%, pH, elemental composition and N-Kjeld to determine which factor (time and/or temperature) has a significant effect ($p\text{-value} \leq 0.05$) on the organic, inorganics and lumped characteristics of wet and dry hydrochar. **Table S3.** P Values of dry and wet hydrochars (from control to week 52) at different temperatures given by analysis of variance (ANOVA) using JMP software. **Table S4.** Results of the one way ANOVA for ICP-OES inorganics (from control to week 52) to determine the effective storage factor, which has a significant effect ($p\text{-value} \leq 0.05$) on these elements in wet and dry hydrochar while in storage. **Table S5.** P Values of inorganics measured by ICP-OES method for dry and wet hydrochars (from control to week 52) at different temperatures given by analysis of variance (ANOVA) using JMP software. **Table S6.** Estimated mass balance on 1 kg of WH considering the concentrations of the compounds in the process liquid which remain in the fresh char and those measured by analysis of the WH. **Fig. S1** Changes in N-Kjeld ($\text{g kg}^{-1}\text{ DM}$) and N measured by elemental analysis of wet and dry hydrochar over storage time (52 weeks). **Fig. S2** Changes in individual: a) sugars, b) acids, c) aromatics of wet and dry hydrochar stored at different temperatures over 52 weeks. **Table S7.** LSD Threshold Matrix of sum of organics given by Dunnett's test performed in JMP software from SAS for total organics in fresh and stored DH and WH over one year of storage. **Fig. S3** Individual values for changes in inorganics (measured by ICP-OES) of wet and dry hydrochar at different temperatures while in storage. **Table S8.** LSD Threshold Matrix of sum of inorganics given by Dunnett's test performed in JMP software from SAS for total inorganics (measured by ICP-OES) in fresh and stored DH and WH over one year of storage. **Fig. S4** SEM and EDX analysis of wet and dry hydrochar stored for 12 weeks at different temperatures. **Fig. S5** The FTIR spectra of a) wet, and b) dry hydrochar over 12 weeks of storage, at different temperatures. **Table S9.** Summary of recommended storage conditions for inorganic measured by ICP-OES method for the DH and WH. The color and coding (0 to nsc) represent the maximum duration for storing samples before observing the first significant changes compared to their control values.

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Author contributions

All authors contributed to the study's conception and design. Material preparation, data collection and analysis were performed by Nader Marzban.

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Data availability

All data generated or analyzed during this study are included in this published article and its additional files.

Declarations

Competing interests

The authors have no competing interests to declare that are relevant to the content of this article.

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