Stability of sewage sludge biochars in soil

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Abstract

Determining the stability of sewage sludge biochar is crucial to ensure its contribution to carbon sequestration. As a primary objective, this thesis work aimed to evaluate the stability of sewage sludge biochars in agricultural soil using established methodologies: chemical oxidation and incubation experiments (92 days) coupled with modelling. Employing these methods yielded an inconclusive assessment of biochar stability. The chemical oxidation using potassium permanganate results indicated that the sewage sludge biochar used in this study is stable, with about 86 % stable biochar C that could persist in soil for around 100 years. However, findings from the 92 days incubation experiment, combined with modelling, suggested that sewage sludge biochar is not that stable (only 7% carbon remaining after 100 years). The inconsistency between both approaches likely owes to the shortness of incubation time and the use of a single first-order model, which is likely to lead to an underestimation of stability. Additionally, the study investigated the potential contribution of carbonates to carbon dioxide emissions and the aim was to differentiate between carbon dioxide emissions originating from organic carbon in biochar and those potentially contributed by carbonates. To accomplish this, the biochar was treated with acid to eliminate carbonates, before incubating both treated and untreated samples. By measuring and comparing the cumulative carbon dioxide emissions from both sets, the carbonate contribution could be isolated. This was done by subtracting the emissions from the treated (carbonate-free) samples from those of the untreated samples, allowing for a more precise evaluation of organic carbon-derived emissions from biochar. Statistical analysis revealed a significant impact of carbonates on carbon dioxide emissions ($p=0.0005$). In future research, the incubation experiment needs to be extended for a longer period (e.g., 1 year) to obtain more reliable estimates of the carbon stability of sewage sludge biochars.

Keywords: biochar stability, sewage sludge biochar, carbonates.

Popular science summary

The project entitled “Testbed Ellinge” aims to produce biochar through pyrolysis of sewage sludge, which could be used as an agricultural soil amendment in Sweden. However, determining the stability of sewage sludge biochar is crucial to ensure its potential contribution to carbon sequestration. This study aimed to analyse the stability of such sewage derived biochar. Determining the stability of sewage sludge biochar is crucial to ensure their potential contribution to carbon sequestration. To achieve this, two well-established methodologies were applied: the chemical oxidation method and the incubation method together with a single first-order model. After chemical oxidation, the percentage of carbon remaining represents the percentage that will remain after 100 years when the biochar is mixed into the soil. For the second method, data from the incubation experiment was fitted by a model to extrapolate the mineralisation rate of the carbon over a future time period of 100 years. Additionally, this study also investigated the potential contribution of carbonates to the carbon dioxide emissions from the incubation experiment.

The biochars used were produced from sewage sludge at three different wastewater treatment plants through pyrolysis at 650°C for 48 hours. Analysis showed that these biochars had a relatively low organic carbon content, high ash content, and a small amount of carbonates. The soil used was a sandy soil with low clay content (<10%) collected from an agricultural field at Ultuna, Uppsala.

The chemical oxidation method indicated that all three biochars were stable, with approximately 86 % of the carbon expected to remain after 100 years. The incubation experiment indicated that the fraction of SSBC mineralised during 92 days of incubation were also low (about 98 % remained). However, modelling gave a different result, suggesting that only around 7 % of SSBC would persist after 100 years. Statistical analysis revealed that carbonates contribute to carbon dioxide emissions during the incubation experiment. These findings align with our expectations based on existing knowledge. However, the incubation experiment was too short to provide accurate long-term stability estimates.

To obtain more robust and quantifiable data on biochar stability, it is crucial to extend the duration of the incubation experiment to at least one year. Prolonging the experiment will provide more reliable long-term estimates and enable a more accurate assessment of sewage sludge biochar stability in the soil environment.

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Abbreviations

SS	Sewage Sludge
SSBC	Sewage Sludge Biochar
WWTP	Waste Water Treatment Plant
BC	Biochar
NT	Non-Treated
T	Treated

1. Introduction

The European Union established the Sewage Sludge Directive (86/278/EEC) in 1986 to promote the safe use of sewage sludge in agriculture. These directives will be updated this year (2024). However, the application of sewage sludge on agricultural soils has been shown to have negative impacts on the environment, including the dispersal and accumulation of organic micropollutants, pathogens, and heavy metals. These concerns have led some countries to take drastic measures, with Switzerland banning the use of sewage sludge in agriculture in 2006 and Germany implementing stringent regulations that make its use economically unfeasible (Wiechmann et al. 2015; Speidel et al. 2015). To address these pollution concerns while still utilizing the potential benefits of sewage sludge such as phosphorus recovery, the municipal association VA SYD in south Sweden is performing a pilot project on sewage sludge pyrolysis. This innovative approach involves pyrolysing the sewage sludge before its application to agricultural fields. As part of this research, the project aims to evaluate the carbon sequestration potential of sewage sludge biochar through this thesis work, potentially paving the way for more sustainable practices in agriculture and waste management in Sweden.

1.1 Benefits and drawbacks of sludge biochar

Adding biochar into soils has been proven to have beneficial effects. For instance, the large surface area of the biochar helps to improve certain properties including the water holding capacity, cation exchange capacity, interaction with soil minerals, serves as a habitat for microorganisms and improve soil structure (Lehmann & Joseph, 2015; Hazrati et al. 2021). However, it is essential to acknowledge that it may still contain trace amounts of organic micropollutants and heavy metals, such as zinc (Zn), copper (Cu), and lead (Pb). These contaminants, if present in significant quantities, could potentially pose risks to the ecosystem in a soil (Zhou et al. 2017). Another drawback of pyrolysing sewage sludge is the potential nitrogen loss during the pyrolysis process, particularly when the process is conducted at elevated temperatures, which is often necessary for optimal results (Lehmann & Joseph 2015).

1.2 Biochar

Biochar is a solid product deriving from the pyrolysis of different kind of organic feedstock material. It is produced through a pyrolysis process, which involves the thermal transformation of organic feedstock in an inert atmosphere or at low levels of oxygen (Racek et al. 2020). Variations in pyrolysis conditions such as treatment temperature, residence time, pressure and oxygen availability can impact the structure of biochar (Lehmann & Joseph 2015; Wiedemeier et al. 2015). Biochar derived from a slow pyrolysis process (minutes to days), and high temperature in absence of oxygen appears to have a high aromaticity compared to those produced by fast pyrolysis, i.e., short residence time (Brewer et al. 2009). Aromaticity is a measure that represents the proportion of aromatic carbon within the overall carbon content of a biochar sample (Lehmann & Joseph 2015). This metric provides valuable insights into the structure and composition of the biochar as well as its stability. The higher aromaticity produced by slow pyrolysis is because the feedstock has more time to undergo a thermal decomposition (Brewer et al. 2009). High aromaticity combined with a high degree of aromatic condensation enhances the stability of biochar (Lehmann & Joseph 2015).

Sewage sludge biochar is produced from feedstock derived from sewage sludge (SS), a complex and diverse material, composed of a mixture of water, minerals and a variety of organic compounds. However, the content of organic compounds of SS is lower than 50 % (Racek et al. 2020). Many organic constituents in SS contains aromatic ring such as organic halogens (AOX), linear alkylbenzenesulfonates (LAS), polyaromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB) and so forth (Lamastra et al. 2018). As a result, the feedstock of the SSBC contains some amount of stable (very slowly degradable) carbon forms. Wiedemeier et al. (2015) reported that feedstock with a higher content of aromatic substances tend to produce biochars with a relatively high aromaticity. During pyrolysis, some elements and volatile substances such as hydrogen, oxygen, phenolic compounds and volatile fatty acids are removed, leaving behind a carbon-rich product primarily consisting of aromatic organic molecules as well as minerals (Chen et al. 2014; Xu et al. 2018; Li & Tasnady 2023). Initially, sewage sludges are dried to reduce moisture content before being subjected to high temperatures in a kiln to produce biochar under different pyrolysis conditions. Pyrolysis also changes the chemistry of the original feedstock as the majority of elements of the feedstock are volatilized. The remaining elements are mostly composed of C-H and C-O groups (Brewer et al. 2009; Wiedemeier et al. 2015). These groups are responsible for the interactions of the biochar with the soil minerals and also with microbes and enzymes.

During the thermal decomposition, small voids form within the biochar structure. This is due to the release of volatile compounds and the breakdown of the original biomass material that results into these small voids (Wei et al. 2022). These small

voids, known as micropores, significantly increase the overall surface area of the biochar at low treatment temperatures (Lu et al. 1995, as cited in Xu et al. 2018). In addition to the micropores, the collapse and condensation of aromatic compounds during pyrolysis creates larger pores, called macropores, within the biochar. The formation of these macropores also contributes to the high surface area of the final biochar product (Lehmann & Joseph 2015). Biochars derived from sludge typically have a high ash content, which may contribute to clogging the pores, reducing the pore volume. However, the pore volume can be restored when impurities like minerals in the ash are leached from it (Hazrati et al. 2021). When biochar is pyrolysed at high temperatures (> 600 ºC), aromatic carbons can condense together, and form clusters called turbostratic aromatic carbon (Keiluweit et al. 2009). A further increase of the treatment temperature to very high treatment temperatures (>1000 ºC) can further increase the aromaticity of the SSBC which eventually decreases the distance of the aromatic carbons and resulting in an increasingly graphite-like structure (Wiedemeier et al. 2015; Lehmann & Joseph, 2015; Brewer et al. 2009; Hazrati et al. 2021). This can potentially lead to a decrease in the surface area of the SSBC (Lehmann & Joseph, 2015; Lu et al. 1995, as cited in Xu et al. 2018).

1.3 Biochar stability in soils

The stability of biochar is directly attributed to its physical and chemical properties, which determine its resistance to biotic decomposition over time. Additionally, biochar's long-term residence in soils is further enhanced by its interaction with soil minerals and its physical isolation within soil aggregates, contributing to its overall recalcitrance in the soil environment (Wiedemeier et al. 2015; Lehmann & Joseph, 2015; Brewer et al. 2009).

The degree of aromatic condensation in biochar is a key physical property that contributes to its resistance to biotic degradation. This is because the aromatic rings in the condensed structure have a very short interplanar distance, forming a compact sheet-like-arrangement. This compact configuration makes the aromatic rings less accessible for decomposition processes, thereby enhancing biochar´s resistance to further degradation (Lehmann & Joseph, 2015; Hazrati et al. 2019). The stability of the aromatic ring is due to the delocalised pi electron system located above and below the six-carbon structure, which makes the entire ring chemically stable and resistant to alteration in various chemical reactions (Hart et al. 2007; Vogt et al. 2011; Lehmann & Joseph 2015). In soil, aromatic carbon structures are primarily degraded by microorganisms. Certain bacteria and fungi, such as Pseudomonas, Alcaligenes, Geobacter and Ferroglobus and others possess metabolic pathways that enable them to degrade aromatic carbon compounds under aerobic as well as anaerobic conditions (Liu 2015). However, the degree to which microorganisms are

capable of degrading highly condensed aromatic structures is still debated (Lehmann & Joseph, 2015).

The stability of biochar is also characterised by its interaction with soil mineral particles. The large surface area and the remaining functional groups, particularly the C-O functional groups, help biochar to chemically interact with soil mineral particles (Lehmann & Joseph 2015; Fan et al. 2023). This interaction leads to the formation of complex structures that makes the biochar less accessible to soil microorganisms (Lehmann & Joseph 2015). Han et al. (2020) discovered that the mineralisation rate of biochar was highest in soils with low clay content, compared to those with high clay content. This finding aligns with the results of Fan et al. (2014), who observed that the mineralisation rate in oxisols—soils rich in iron (Fe) and aluminum (Al) oxides—was significantly lower than in Inceptisols, Entisols, and Vertisols (i.e because of the predominant negative charge on these soil surfaces). The underlying reason is that the negatively charged biochar can interact with the positively charged iron (Fe) and aluminum (Al) oxides, forming complex structures that protect the biochar from interaction with soil microorganisms or enzymes, thereby stabilising the biochar carbon in the soil. Additionally, a physical isolation can also help to protect the biochar from degradation and decomposition. Biochar that becomes embedded within soil aggregates will be physically isolated from soil microorganisms and enzymes. Such protection would increase the residence time of the biochar in the soil and potentially enhance the long-term carbon sequestration potential (Yang et al. 2018).

1.4 Methods to determine biochar stability

There are several methods for assessing biochar stability according to the International Biochar Initiative (IBI) (Budai et al. 2013), which involves biochar carbon stability proxy indicators, chemical oxidation resistance determination and biochar persistence evaluation by incubation and modelling.

1.4.1 Biochar carbon stability proxy indicators

This method involves the study of biochar properties related to its stability, such as the H/Corg (hydrogen to organic carbon) and O/Corg (oxygen to organic carbon). The correlation between H/C and O/C ratio to the percentage of biochar carbon remaining after 100 years (BC100) provide a qualitative and conservative indication of biochar carbon stability in soils. Biochars with relatively lower H/C and O/C ratios are more recalcitrant because they generally have higher aromaticity compared to biochars with high H/C and O/C ratios (close to 0.7 and 0.4 respectively) (Budai et al. 2013). Spokas (2010) found that biochars with an O/C

ratio below 0.2 are the most stable, with an estimated half-life exceeding 1000 years. Biochars with an O/C ratio between 0.2 and 0.6 exhibit intermediate stability, having a half-life between 100 and 1000 years. In contrast, biochars with an O/C ratio greater than 0.6 are considered unstable, with a half-life of less than 100 years. Additionally, nuclear magnetic resonance (NMR), pyrolysis gas chromatography/mass spectrometry, or benzene polycarboxylic acid (BPCA) analysis are other methods for studying the structure of biochar carbon. Very recently, the random reflectance (Ro) method was proposed by Sanei et al. (2024) as an effective tool for accurately estimating inertinite content in biochar (long-term stable carbon), which reflects the degree of aromatic condensation and overall stability of the biochar.

1.4.2 Biochar oxidation resistance determination method

This method accelerates the decomposition process of biochar by oxidising the biochar carbon with an oxidising agent like hydrogen peroxide (H_2O_2) or potassium permanganate ($KMnO_4$) (Crombie et al. 2013; Cross & Sohi 2013; Leng et al. 2019; Tirol-Padre & Ladha 2004). If a high amount of biochar carbon mass remains after the oxidation treatment, it indicates that the biochar contains a high amount of stable forms of carbon. For instance, Cross & Sohi (2013) have developed a hydrogen peroxide (H_2O_2) oxidation method that the authors claim simulates around 100 years of natural decomposition in temperate environments.

1.4.3 Soil incubation and modelling method

This methodology involves incubation experiments where soil is mixed with biochar and incubated in an airtight jar and the CO_2 emissions from the incubation are measured over time. The CO_2 emissions from the biochar is calculated by subtracting the CO_2 emitted in the control from CO_2 emitted in biochar-amended soil samples. The CO_2 emissions data or the carbon remaining data from incubation can be fitted by an exponential decay model in order to derive a degradation rate for the biochar (or several rates if it is a multiple pool model). The key parameters that are usually estimated are the mean residence time (MRT), the half-life of the carbon or the percentage of biochar carbon that is predicted to remain after 100 years (BC100). When choosing a model, it is important to consider the potential presence of different carbon pools within the biochar. According to Lehmann & Joseph (2015) and Li & Tasnady (2023), modelling approaches can involve one-pool, double-pool, triple pool or infinite-pool models with varying levels of complexity. When specifying the degradation kinetics, these models are also known as single first-order model (SFO), double first-order models (DFO), triple firs-order models (TFO) and power model (Azzi et al. 2024).

Single first-order models assume an average degradation rate for the entire biochar carbon content, treating it as a single homogeneous pool. SFO model yields one first-order mineralisation rate constant. In double first-order models, the biochar carbon is divided into two pools: a labile (readily degradable) pool and a stable (recalcitrant) pool. The degradation of the pools are assumed to follow first-order kinetics even though the degradation rates are different. A power model assume that biochars consist of a continuum of carbon compounds of variable degradability (Zimmerman 2010). In a new study, the power model is recommended to use for calculating biochar persistence in soil, although it was found to be sensitive to the quality of the dataset (Li et al. 2024).
As the complexity of models increases from SFO to power models, the accuracy of the estimations generally improves. However, more complex models may require additional data and computational resources. The choice of model depends on the specific application, available data, and the desired level of accuracy in predicting biochar carbon stability. Additionally, factors like incubation duration and data quality can also influence the choice of the modelling method (Li & Tasnady 2023). Choosing an appropriate model is critical to estimate biochar stability in soil (Azzi et al. 2024).

1.5 Contribution of carbonates to CO_2 emissions from biochar in soils

Carbonates are inorganic carbon compounds that naturally occur in soils; however, sludge biochar also contains a certain amount of carbonates originating from the pyrolysis process. These carbonates are formed during pyrolysis at high temperature when alkali elements like Na, Mg, Ca, K, Fe react with CO_2 (Tomczyk et al. 2020). During the incubation, carbonates can dissolve and contribute to CO_2 emissions from the incubation. If the carbonate-derived CO_2 is not compensated for, the long-term persistence of the organic carbon in the biochar is likely to be underestimated because the release of CO_2 from carbonates is chemical reaction rather than the microbe-mediated process. Data from this release of CO_2 can have a lot of weight when fitting it to a degradation model.

1.6 Objectives and hypotheses

The first objective of this thesis was to investigate the stability of carbon in sewage sludge biochar, produced using sludge from three different wastewater treatment plants to ensure representativeness, when applied to agricultural soil. This investigation employed both incubation and chemical oxidation methods. The

second objective was to study the contribution of carbonates to total CO_2 emissions in sludge biochar amended soils.

As the biochar was derived from sewage sludge and pyrolysed at high temperature (650 ºC), the hypothesis was that the organic carbon fraction would be highly resistant to degradation when applied to soil, because of a high aromaticity in the biochar. We also hypothesised that the carbonate in SSBC would contribute significantly to overall CO_2 emissions, particularly at the onset of incubation.

2. Materials and methods

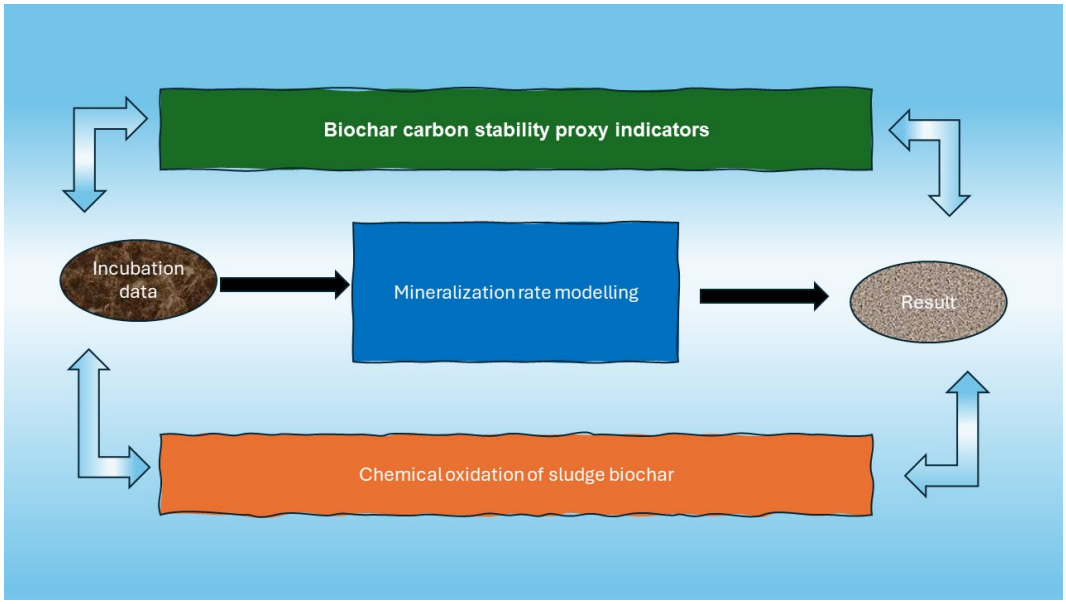

Figure 1. Conceptual figure providing an overview of the method of this study.

2.1 Soil

The soil was collected from an agricultural field at the onset of the 2023/2024 winter season close to Ultuna Campus, Uppsala. It is a loamy sand with 80.2 % sand, 9.6 % silt and 10.2 % clay. The soil pH was measured to be 5.03 (soil:$CaCl_2$ 1:5) and the percentage of soil organic carbon to be 1.4 %. The samples were stored in a freezer room maintained at -20°C. At the start of the experiment, the frozen soil was removed from the freezer and allowed to gradually thaw at room temperature (22°C) and the soil was then processed through a series of sieves. First, it was passed through a 4 mm mesh screen to remove larger stones and plant residues. Subsequently, it was sieved again using a 2 mm mesh to further break down soil aggregates and obtain a consistent, homogeneous sample. The aim of this preparation was to ensure that the soil contained a homogenous particle size for experimental analysis while preserving its natural characteristics as closely as possible.

2.2 Sewage sludge biochar (SSBC)

Three different SSBC originating from three different wastewater treatment plants (WWTP) located at Fårevejle, Höjby and Nyköping district in Denmark, were provided by Dr David Gustavsson at VA SYD (water and sewage management association in the southern part of Sweden). The treatment temperature reached approximately 650°C and the residence time was around 48 hours for the three SSBC, falling under the category of slow pyrolysis as defined by Racek et al. (2020).

2.3 Acid-treated sludge biochar

In order to eliminate the carbonates in the sludge biochars, the abovementioned biochars were pre-treated with 0.1 M hydrochloric acid (HCl). The pre-treatment process for the SSBC sample was carried out as follows: 20 mL of deionised water was added to 2 g of SSBC, and the mixture was left for 1 hour. Then, 1 mL of 0.1 M HCl was added to the biochar suspension, and the samples were left for 1 hour after the HCl addition. The pH value of the treated biochar suspension was measured, and this systematic pre-treatment process was repeated over a period of 200 hours, with the pH being monitored until it stabilized at around 5.5. Sustaining the biochar's pH at this specific level indicates that the carbonates have been removed from the SSBC material. For the SSBCs that were not treated with acid, 30 g of each SSBC was mixed with 300 mL deionised water instead. The samples were oven dried for 24 hours, and finally collected and stored in sealed plastic bags.

2.4 Incubation

The three sludge biochars and the corresponding three acid-treated biochars were mixed with soil at rate of 2% on dry mass basis. One control without biochar amendment was also included, thus totalling 7 treatments. Each set consisted of 5 replicates, resulting in a total number of 35 samples. An addition of three blanks, i.e only sodium hydroxide (NaOH) solution was also included to quantify the CO_2 present in the jars before incubation. The soils mixed with biochars and the control soil were packed to a bulk density of 1.2 g/cm^3. The container of each sample was labelled and weighed. 1.88 g (2 % of dry soil) of SSBC was mixed with 108.6 g field moist soil in a plastic tube (height: 10 cm, diameter: 5 cm) and the soil was kept at 60 % water holding capacity (WHC) by adding deionized water to it when replacing the NaOH solutions. The experiment was conducted for 92 days during which a total of eight measurements were conducted.

Figure 2. Incubation jars setup.

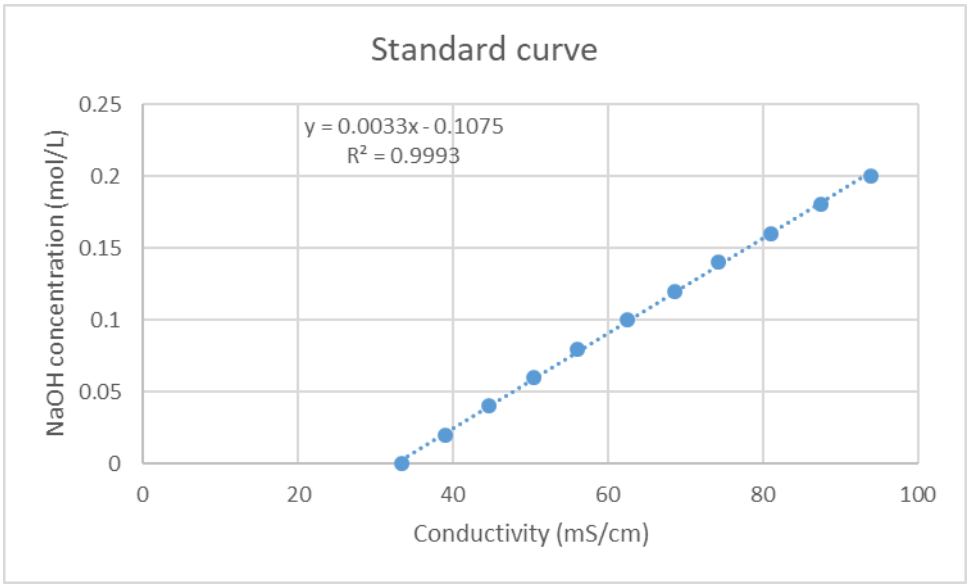

Figure 3. Standard curve of concentration of sodium hydroxide vs conductivity.

2.5 CO_2 measurement

Each soil sample and 50-ml centrifuge tube containing 20 ml of 0.2 M NaOH solution were placed into airtight glass jars (Figure 2). These jars were incubated at a constant temperature (20 °C) for 24 hours. To ensure that the jars were airtight, a solution of sodium hydroxide (NaOH) was stored in each jar for 24 hours prior to the start of the experiment, after which the NaOH solutions were collected, and

their conductivity was measured. The purpose of this process was to detect any potential leaks in the jars, as exposure to air can affect the conductivity of the NaOH solution and potentially lead to errors.

At each measurement session, the conductivity was measured in the collected NaOH solutions to calculate the CO_2 trapped inside. To quantify the amount of carbon dioxide trapped in the NaOH, a calibration curve between the NaOH concentration and solution conductivity was established. NaOH was gradually replaced with Na_2CO_3 in these solutions to represent a higher amount of CO_2 being trapped in the NaOH solutions used during incubations described by Equation (1). The standard curve (Figure 3) was developed using a total of 11 known concentrations of NaOH, ranging from 0.2M NaOH at the beginning when Na_2CO_3 is still 0 M to 0 M NaOH at the end when all CO_2 have reacted with NaOH and formed 0.1 M Na_2CO_3. The conductivity of these samples was measured, and the concentration-conductivity data points were used to construct the calibration curve. From this calibration curve, a mathematical equation was derived that describes the relationship between NaOH and CO_2, (Equation 2). This equation was then used to calculate how much NaOH had been consumed during the incubation process.

$$2NaOH + CO_2 \leftrightharpoons Na_2CO_3 + H_2O \quad (1)$$

The equation from the calibration curve represents a linear function as described by Equation 2.

$$y = 0.0033x - 0.1075 \quad (2)$$

2.6 Biochar C mineralisation rate and modelling

To determine CO_2 emitted from biochar, we assumed that the biochar derived CO_2 equals the total CO_2 emissions from soil mixed with SSBC minus CO_2 emissions from the control. To track the gradual increase of CO_2 emissions from the biochar samples during incubation, we calculated the cumulative CO_2 by adding each new quantified amount of CO_2 to the previously calculated total. This approach allowed us to observe the gradual accumulation of CO_2 and establish the mineralisation curve, illustrating the amount of organic C from the SSBC that was emitted as CO_2 over time.

The mineralisation rate can also be illustrated by plotting the percentage of carbon remaining over time. To calculate this, we subtracted the amount of carbon emitted as CO_2 from the initial organic carbon content at the start of the incubation. This difference was then divided by the initial carbon content, resulting in the percentage of carbon remaining.

The mineralisation rate obtained from the incubation experiment can be fitted to a decay function (see Equation 3, 4, 5) in order to exhibit the decomposition pattern of the biochar. If the curve is well fitted in the decomposition pattern, it can be

extrapolated to longer time scale in order to estimate the carbon stability. The estimated time scale is often 100 years, also known as BC100.

Equation of a single first-order (SFO) model is presented in Equation 3 where k is the degradation rate, X is the time and a is the initial biochar carbon. Y is the remaining biochar carbon at time X.

$$Y = a^{(-b*X)} \quad (3)$$

Equation of a double first-order (DFO) model is presented in Equation 4 where b is the degradation rate of the labile carbon pool and d is the degradation rate of the stable carbon pool, X is the time and a is the initial biochar carbon of labile pool, c is the initial biochar carbon of stabile pool. Y is the remaining biochar carbon at time X.

$$Y = a^{(-b*X)} + c^{(-d*X)} \quad (4)$$

Equation of a power model is presented in Equation 5 where m is the slope, b is the intercept, t is the time and C_0 and C_t are the initial carbon and the remaining carbon at time t (Zimmerman, 2010).

$$C_t = C_0 - \left(\frac{C_0 * e^b}{m+1}\right) * t^{m+1} \quad (5)$$

2.7 Chemical oxidation by hydrogen peroxide (H_2O_2)

In this experiment, hydrogen peroxide (H_2O_2) was used as an oxidising agent to determine the stable carbon of SSBC in accordance with the method used by (Cross & Sohi, 2013). A total of nine samples were analysed, with three replicates for each sample. The first group of samples were collected from acid-treated biochars, the second group were from untreated biochar, and the third group consisted of the feedstock for each biochar. The mass of each sample was determined based on the organic carbon content. For each sample, 7 mL of 0.01 M hydrogen peroxide (H_2O_2) was added into 0.1 g C equivalent biochars or feedstocks, and the entire collection was placed in a water bath maintained at a temperature of 80°C. The samples were left to run for a duration of 48 hours, with the samples being shaken two to three times per day. After 48 hours, the samples were collected and put in an oven to get dried. An analysis was then conducted by Soil and plant laboratory at the Swedish University of Agricultural Sciences, to determine the carbon content of the remaining material. The method used for the analysis was, the dry combustion method using a CN analyser from Leco Corp. This method follows the ISO10694 (1995) standard for determining organic carbon in soils. It should be noted that the concentration of the hydrogen peroxide used in the experiment was underestimated. This was not discovered until very late in the thesis work, at which point it was too late to repeat the experiment.

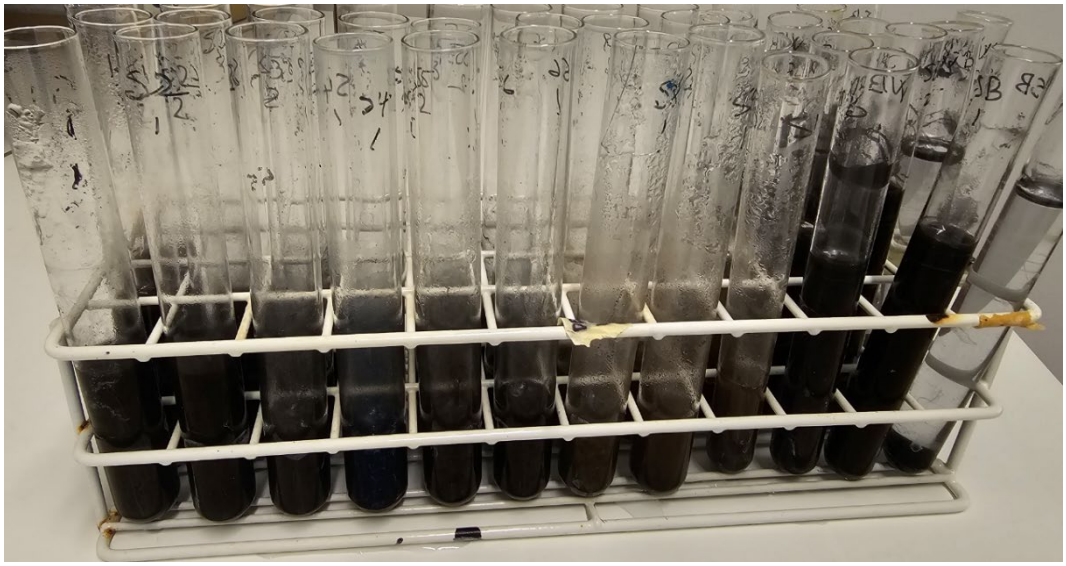

Figure 4. SSBC/SS mixed with hydrogen peroxide solution.

2.8 Chemical oxidation by potassium permanganate ($KMnO_4$)

This experiment was conducted in accordance with the method used by Tirol-Padre & Ladha (2004). In this experiment, six samples of biochar and three samples of sewage sludge, three replicates each, were set up. Additionally, one blank with three replicates was also set up. The mass of each sample was determined according to the organic carbon content (0.1 g C equivalent) and 25 mL 33 mM potassium permanganate was added. The samples were then placed in a shaker and shaken for 48 hours. After the shaking process, the samples were collected, diluted twenty times and their absorbance was measured using a spectrophotometer at a wavelength of 565 nm. The experiment was repeated with the same procedure using half the amount of substrate of the first trial and the aim of this subsequent trial was to make any potential differences more apparent.

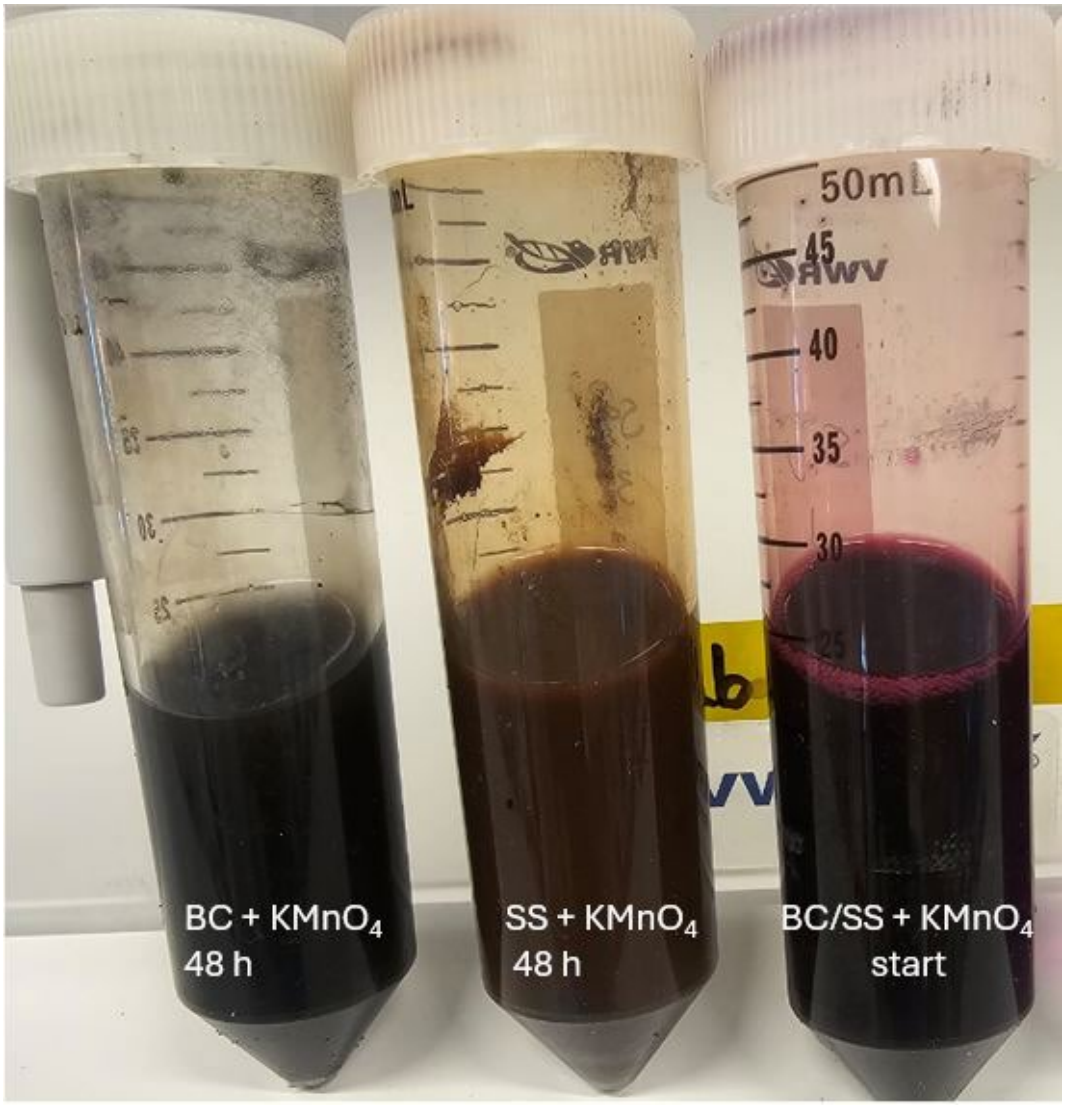

Figure 5. SSBC/SS mixed with potassium permanganate solution.

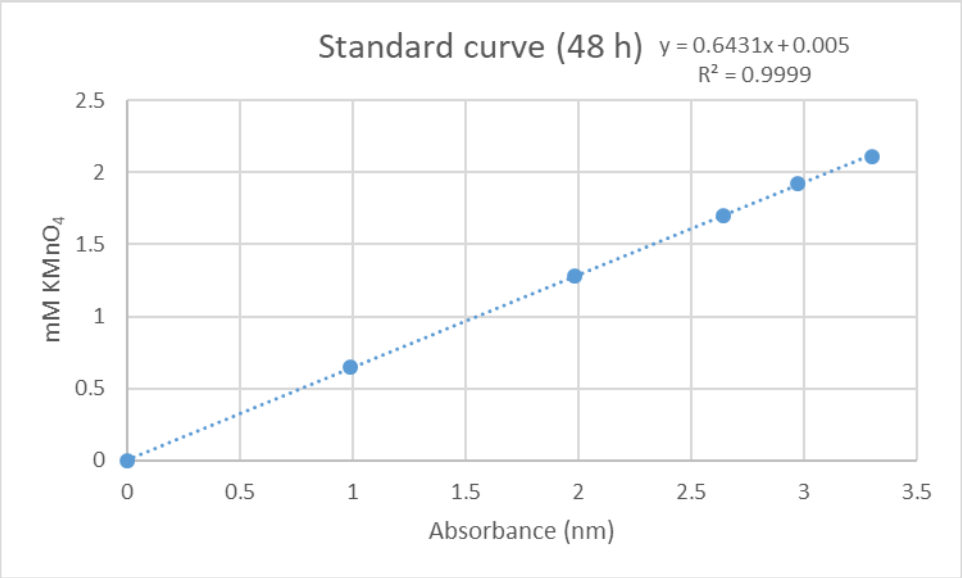

Figure 6. Standard curve after 48 h chemical reaction of $KMnO_4$ and C of substrate.

2.9 Statistical analysis

One-way analysis of variance (ANOVA with a confidence level of 0.05) was used to investigate if there were significant differences between the treated SSBC and the untreated SSBC. This was done using Rstudio software version 2024.

3. Results

3.1.1 Biochar properties and stability proxy indicators

Results from the biochar property analysis conducted by Eurofins Umwelt in Germany are presented in table 1. The H/C and O/C ratios for the biochars from Fårevejle WWTP and Nyköbing WWTP were nearly identical, at 0.44 and 0.45 respectively, whereas the biochars from Höjby WWTP had higher ratios of 0.54 and 0.55. The organic carbon content for the biochars from Höjby WWTP and Nyköbing WWTP was similar, both at 25.2% (dry basis), while the biochars from Fårevejle WWTP had a slightly higher organic carbon content of approximately 28.4% (dry basis). Additionally, Höjby WWTP and Nyköbing WWTP showed similar ash content, around 65%, whereas Fårevejle WWTP had a lower ash content of about 61%. The pH values and carbonate content of the biochar from all three WWTP were also similar, with pH around 7 and carbonate content approximately 2%.

Table 1. Sludge biochar properties analysis for Fårevejle, Höjby and Nyköbing WWTP.

Parameter (Fårevejle)	Unit	Value (dry basis)
Moisture	% (w/w)	-
Ash content (55°C)	% (w/w)	61.9
Total carbon	% (w/w)	29.0
Organic Carbon	% (w/w)	28.4
Carbonates- CO_2	% (w/w)	2.1
H/C ratio	N/A	0.44
O/C ratio	N/A	0.45
pH in $CaCl_2$	N/A	7.5
Parameter (Höjby)	Unit	Value (dry basis)
Moisture	% (w/w)	-
Ash content (55°C)	% (w/w)	65.2
Total carbon	% (w/w)	25.8
Organic Carbon	% (w/w)	25.2
Carbonates- CO_2	% (w/w)	2.1
H/C ratio	N/A	0.54
O/C ratio	N/A	0.55
pH in $CaCl_2$	N/A	7.2
Parameter (Nyköbing)	Unit	Value (dry basis)
Moisture	% (w/w)	-
Ash content (55°C)	% (w/w)	65.5
Total carbon	% (w/w)	25.9

Organic Carbon	% (w/w)	25.2
Carbonates- CO_2	% (w/w)	2.5
H/C ratio	N/A	0.44
O/C ratio	N/A	0.45
pH in $CaCl_2$	N/A	7.3

3.2 Chemical oxidation

3.2.1 Hydrogen peroxide

The results from the chemical oxidation test using hydrogen peroxide, as illustrated in Figure 7, suggested that all SSBC were very stable despite the low estimation of H_2O_2 concentration. The untreated SSBCs exhibit a maximum carbon loss of merely 1.5% (i.e 98.5 % carbon remaining), while the acid-treated samples displayed an even lower loss of 0.5% (i.e 99.5 % carbon remaining). In contrast, the sludge materials lost a comparatively greater amount of carbon of approximately 5% (i.e 95 % carbon remaining) during the oxidation process. Please note that the results are likely not reliable because the H_2O_2 concentration was underestimated.

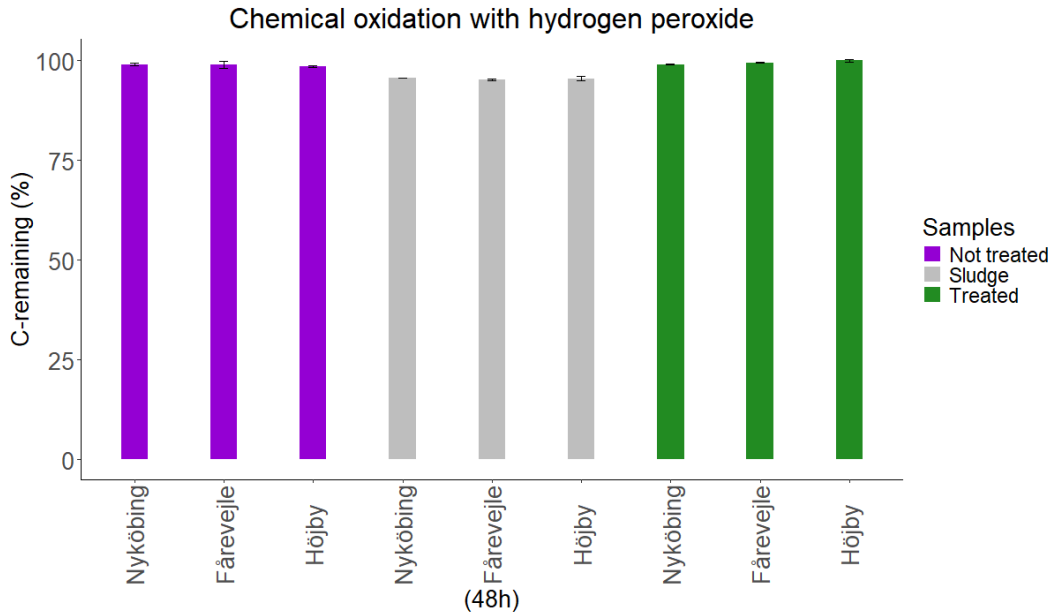

Figure 7. Chemical oxidation using hydrogen peroxide. The charts are color-coded to differentiate between the various substrates under analysis. The green bars denote SSBC that has been treated with acid and the purple represent the untreated SSBC. Finally, the grey bars correspond to sewage sludge. Error bars denote standard errors (n=3).

3.2.2 Potassium permanganate

The results from the chemical oxidation using potassium permanganate are presented in Figure 8, and it shows that the SSBC material is relatively stable. The carbon loss for the SSBC generally decreased down to 92 % carbon remaining, while the sludge experienced a more significant loss. The carbon remaining in figure 8A is relatively even (92 %) for all samples. However, when reducing the amount of substrate by half, the SSBC experienced a higher carbon loss with 86 % carbon remaining for the biochar, and 72 % carbon remaining for the sludge (Figure 8B).

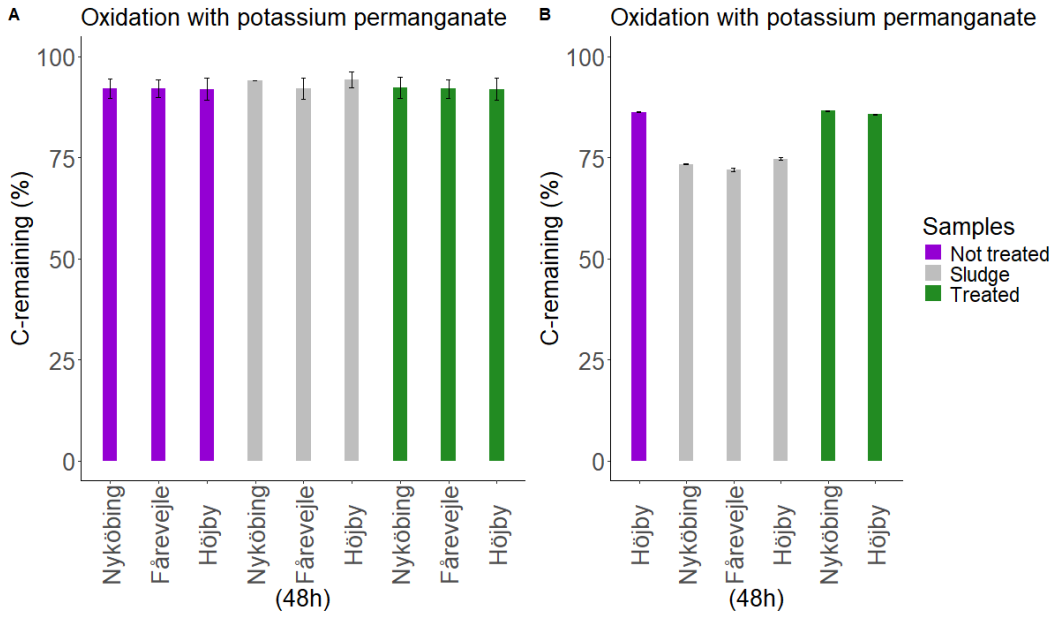

Figure 8. Chemical oxidation using potassium permanganate ($KMnO_4$). (A) shows the result of the chemical oxidation and (B) Shows the result from the chemical oxidation using half of the amount of substrate used in A (Note! some samples have been omitted). Error bars denote standard errors (n=3).

3.3 Incubation and modelling

The results from incubation experiment are shown in Figure 9. It shows the cumulative CO_2 emitted during the 92 days incubation. While the cumulative CO_2 increases, reflecting the release of carbon from SSBC, the residual carbon mass of the SSBC decreases correspondingly.

A general trend observed in the charts of Figure 9 is as follows: the non-treated SSBC from Fårevejle, Højby, and Nyköbing in the top chart exhibits higher cumulative carbon levels (70, 120, and 100 mg C-CO_2/kg soil, respectively) compared to the treated SSBC (85, 65, and 45 mg C-CO_2/kg soil, respectively). Additionally, the bottom chart of Figure 9 indicates a difference in residual biochar

carbon, with non-treated SSBC showing lower residual carbon percentages (98%, 97%, and 98%) compared to treated SSBC (99% on average).

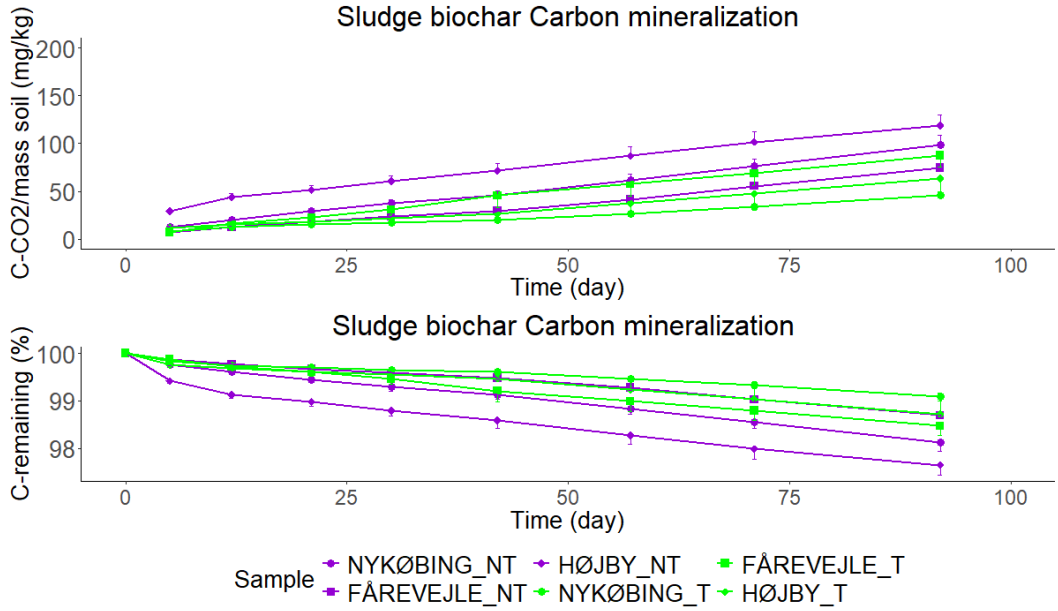

Figure 9. Incubation data showing the cumulative CO_2 (chart on top) and the percentage carbon mass remaining (chart on the bottom). The abbreviations in the legend are as follow: NT means non-treated (i.e SSBC that are not treated with HCl), T means treated (i.e SSBC that have been treated with HCl) Error bars denote standard errors (n=5).

The results of the mineralisation rate modelling are presented in Figures 10-11. Figure 10 shows the curve fitting of the mineralisation rate for Fårevejle SSBC which was similar to the two other SSBCs. Fitting the mineralisation rate to the single SFO model showed good patterns as expected but fitting to DFO model resulted in very large standard errors of the estimated parameters and the power model yielded unrealistic estimations (negative values, Fig. 10). Therefore, the SFO model was used for further extrapolation. The results obtained from the extrapolation of the SFO-model are illustrated in Figure 11 and it indicates that the SSBC carbon is not stable. The non-treated SSBC exhibited a relatively low remaining SSBC carbon mass, with only approximately 2% of the initial carbon content persisting after 100 years. Also, the treated SSBC displayed a low remaining carbon mass, with around 7% of the original carbon mass remaining intact after 100 years (Figure 11).

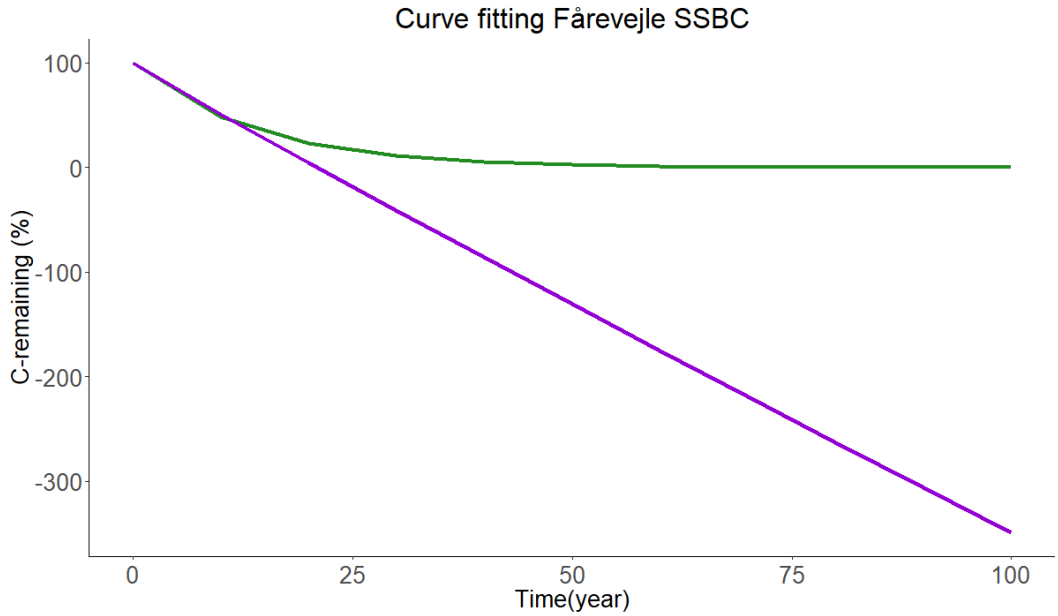

Figure 10. The graph illustrates mineralisation rate curve fitting for Fårevjele SSBC, comparing two distinct models. The Single First-Order (SFO) Model, represented in green, exhibits a constant rate of decrease for the initial 25 years before stabilizing and maintaining a steady state from 25 to 100 years. The Power Model, shown in dark purple, demonstrates an unrealistic 100-year estimation.

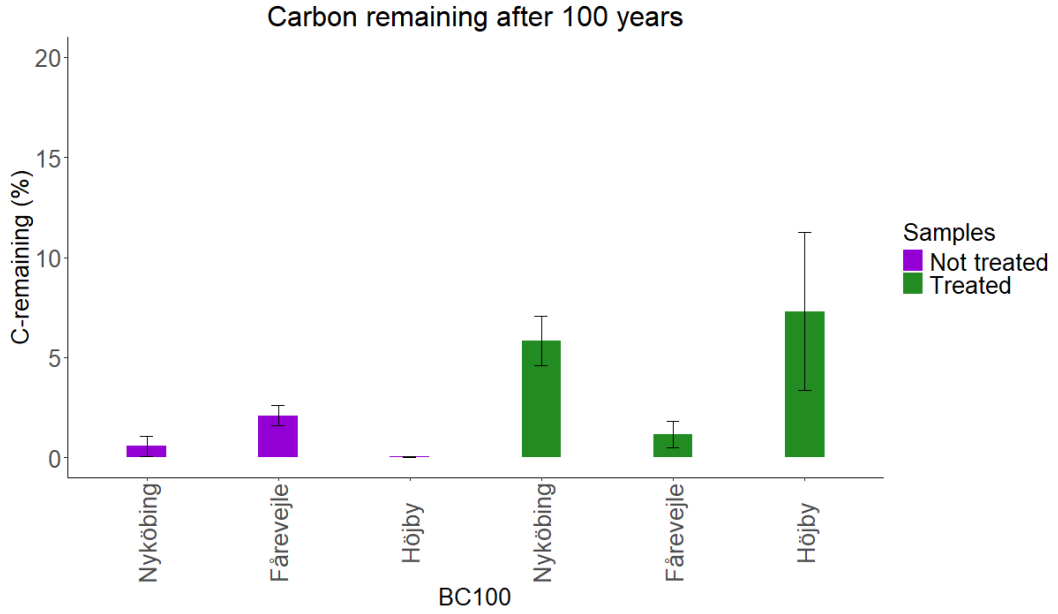

Figure 11. Percentage of SSBC carbon remaining after 100 years estimated by a single-first order model. The dark purple bars represent the non-treated SSBC and the green represent the treated SSBC.

3.4 Potential carbonate contribution

The potential carbonate contribution of the three SSBC is illustrated in Figure 12. The graph shows the carbonate contribution for each SSBC over the incubation period. The carbonate contribution for Nyköbing SSBC increases at a constant rate throughout the incubation period but for Höjby it does increase in the beginning but slows down at the end. In contrast, SSBC from Fårevejle seems to exhibit a negative contribution of the acid treatment at the beginning and then no difference the rest of the incubation. The cumulative carbon in both Höjby and Nyköbing was about 55 mg C-CO_2/kg soil but for Fårevejle, the cumulative contribution was about -10 mg C-CO_2/Kg soil. Additionally, the statistical analysis revealed a statistically significant difference between the SSBC treated with acid and the SSBC group that did not receive the acid treatment. The calculated p-value was 0.0005.

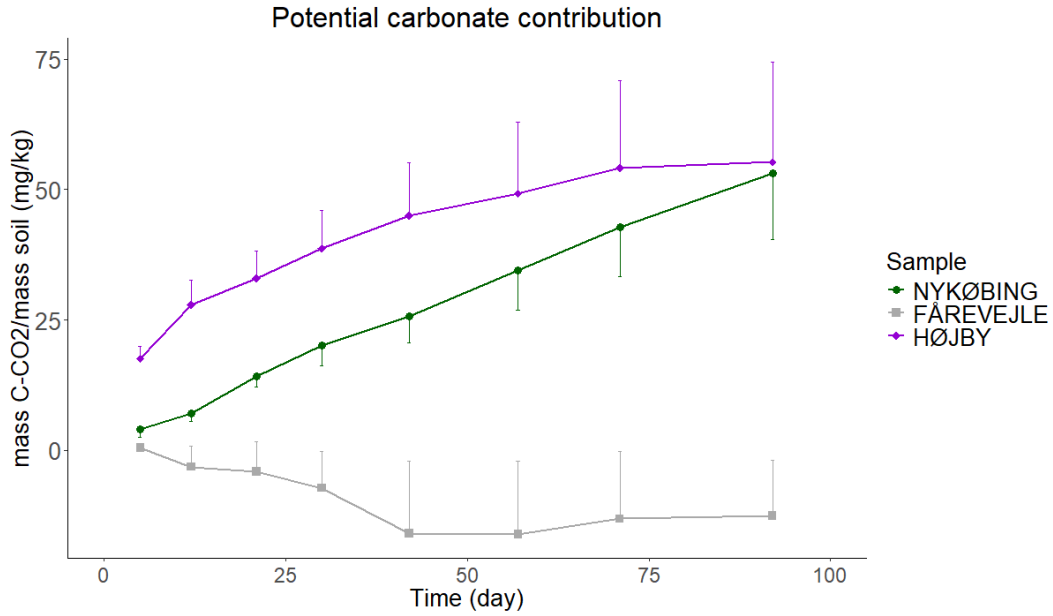

Figure 12. Cumulative difference in CO_2 emissions between treated and non-treated biochar from different treatment plants. Error bars denote standard errors (n=5).

4. Discussion

4.1.1 Biochar stability proxy indicators

The analysis of biochar properties indicated that the biochar can be classified as stable according to the criteria used by Spokas (2010) to define the stability of biochar products. The H/C ratio ranged from 0.44 to 0.54 (dry basis) across all three WWTP, which falls within the intermediate range of data published by Azzi et al. (2024). However, the O/C ratio of the biochar, varying between 0.45 and 0.55 (dry basis) for the three WWTP, is relatively high compared to the data reported by Azzi et al. (2024) but according to Spokas (2010) it is within intermediate range.

4.1.2 Chemical oxidation and incubation followed by modelling

The chemical oxidation experiments in this study indicated that the SSBC used is stable. After treatment with potassium permanganate, 86 %- 92 % of biochar C remained. This indicates that a significant portion of the biochar carbon is resistant to chemical degradation. The carbon loss from the chemical oxidation using hydrogen peroxide showed very small changes (< 2 % SSBC carbon loss), which is significantly lower compared to previous studies. This small carbon loss must be due to the underestimation of the concentration of hydrogen peroxide used in this experiment. For instance, Cross & Sohi (2012) reported a carbon loss of about 35% for a chicken manure biochar, using a 1.43 M H_2O_2 compared to the concentration used in this study (0.01M H_2O_2).

The residual carbon in Figure 8A was higher than the residual carbon in Figure 8B (92 % and 86 % respectively) and the reason behind is because the amount of carbon used to run the experiment in Figure 8A was twice higher than the amount used in Figure 8B. From a stoichiometric perspective, this indicates that the number of moles of $KMnO_4$ was less than the number of moles of C in Figure 8A compared to Figure 8B. However, during the shaking process involved in this trial, an accidental leakage occurred, resulting in the loss of several samples. Consequently, the only remaining samples available for analysis are those depicted in Figure 8B.

The patterns observed in the incubation experiment for mineralisation rate and decomposition rate align well with each other and with previous studies. As shown in Figure 9, the mineralisation rate increases in a manner that mirrors the decrease in decomposition rate over time. This correlated trend is consistent with findings from even longer incubation experiments conducted by Budai et al. (2013) and Kuzyakov et al. (2014). The relatively rapid increase in mineralisation rate from the start of the experiment can be attributed to the labile carbon pool present in the samples, as explained by Lehmann & Joseph (2015). The labile carbon compounds

are readily broken down and mineralised first, leading to the initial spike in mineralisation rate before slowing down as more recalcitrant carbon remains.

The biochar C remaining estimates using the power model were unrealistic given the negative values. This could be explained by the fact that the power model is sensitive to the initial mineralisation rate of the incubation experiment (Li et al. 2024). SFO-model was used to extrapolate the mineralisation rate and the results indicated that the SSBC used in this study is not stable. However, it is important to note that the incubation lasted for 92 days, which is likely insufficient for accurately assessing the long-term stability of the SSBC. The findings from previous studies suggest that longer incubation periods, ranging from one to two years or even longer, are necessary to obtain reliable results on biochar carbon mineralisation rates and stability. Zimmerman (2010) found that the mineralisation rate of an incubation experiment decreases with time and stabilises after reaching 600-700 days. The initial high mineralisation rate observed in the first few months of incubation experiments may not reflect the long-term behaviour of biochar in the environment. In a biochar stability study conducted by Wang et al (2015), it was found that the mean biochar decomposition rate for studies with a duration of less than 0.5 years is approximately four times greater, compared to the mean decomposition rate from studies lasting longer than 1 year. As the incubation progresses, the mineralisation rate tends to decrease and stabilise, indicating the presence of a more recalcitrant fraction of biochar that persists over longer timescales. Kuzyakov et al. (2014) have studied CO_2 emissions from incubation experiment using ^{14}C labelled biochar during a period of 8.5 years and the results from that experiment showed that most of the $^{14}CO_2$ released from the incubation was during the first 2 years. The initial high mineralisation rate can also be explained by the priming effect (Han et al. 2020).

The choice of modelling method is crucial for obtaining reliable estimates of biochar stability in soil. The large variations indicate how the model choice can significantly influence the predicted stability of biochar carbon in soil systems. As the incubation time was relatively short (92 days), it was not possible to fit our data to a double-pool model or a power model. Therefore, a single pool model was used to estimate the carbon remaining after 100 years (BC100). However, we must interpret the data with great care since we know a priori that single first-order models cannot possibly accurately predict the future mineralisation of a biochar consisting of a labile and a stable pool which is often the case. The stable pool represented about 85 % residual carbon from the $KMnO_4$ experiment. Therefore, longer incubation data are needed in future research.

The difference in CO_2 emissions between non-treated samples and treated SSBC samples from Nyköbing and Höjby (Figure 12) indicates a potential contribution from the carbonates. This can also be observed in Table 1, which reveals that the ash content of these two SSBCs was highest among the three SSBCs analysed.

Biochars with high ash content contains carbonates (Leng et al. 2019). Brunn et al. (2014) as cited in Sun et al. (2022) stated that carbonates from soil-derived biochar (SSBC) can decompose rapidly, leading to higher CO_2 emissions, particularly in the initial stages of incubation experiments. Against our expectation, carbonate in biochar still contributes CO_2 emission even after 3 months especially for Nyköbing SSBC. For SSBC from Höjby, the CO_2 emission from the carbonates slowed down to almost no increase at the end and this means that most carbonates were released early and are gradually exhausted. This was the most expected pattern of carbonate contribution to CO_2 emission. The carbonate CO_2 emission pattern of Fårevejle SSBC indicates no contribution of carbonates. Overall, our results suggest that carbonates in biochars can be a critical source that accounts for CO_2 emission (for instance, approximately 55 mg/kg soil in Höjby and Nyköbing after 92 days) when adding biochar in soil. Thus, to accurately estimate long-term biochar persistence in soil, it must be distinguished from biochar mineralisation.

4.1.3 Limitations and future directions

One limitation of this study is the reliance on a relatively short incubation period to assess biochar stability. While short-term incubation studies can provide valuable initial insights, they may not accurately capture the long-term stability and degradation processes of biochar in soil. For instance, biochar interaction with soil minerals and encapsulation of biochar particles, are processes that occur gradually and take long time to develop fully, after biochar is mixed with the soil. Additionally, the study did not possess other tools to differentiate the CO_2 sources. For instance, biochar addition to the soil can result in a priming effect, which could be difficult to capture by only using a control sample as a reference. Han et al (2020) found that biochar addition to sandy soils greatly increased the mineralisation rate of soil initial organic carbon. For future studies, isotopic measurement of released CO_2 could be used to differentiate between the CO_2 released from the biochar, soil organic matter, the carbonates and the carbon that has ended up in the microbial biomass. This method have been proven to give more accurate results (Kuzyakov et al. 2014). However, even if this is possible, its implementation can be technically challenging and very expensive. Moreover, since the microorganisms are the driving force for biochar C mineralisation, measurements of microbial parameters would be useful for data interpretation. As Leng et al. (2019) pointed out, the decrease in mineralisation rate may be a result of changes in the microbial biomass.

5. Conclusion

This study demonstrates the potential of sewage sludge biochar for carbon sequestration and soil amendment applications. The key findings can be summarized as follows: Chemical oxidation treatment indicated high stability, with approximately 86% of the biochar carbon expected to persist in soil for around 100 years. However, the 92-day incubation experiment and modelling suggested lower stability, with only 7% of the carbon remaining after 100 years, likely due to the relatively short incubation period in combination with the use of a single first-order model. Statistical analysis revealed that carbonates may contribute to CO_2 emissions from the sludge biochar. While this study provides valuable insights, it is essential to acknowledge its limitations, particularly the relatively short incubation time. To obtain more robust and quantifiable results regarding the long-term stability of sewage sludge biochar, we suggest keeping soil incubation over extended periods, such as one year as well as performing microbial analyses and if possible, use ^{13}C labelling to better understand biochar persistence in the soil.

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