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Pyrolysis of Sewage Sludge as a Method of Carbon Sequestration into Soil

Bachelor thesis

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Declaration

      I declare that my bachelor thesis titled "Pyrolysis of Sewage Sludge as a Method of Carbon Sequestration into Soil" is the result of my independent work under the guidance of my thesis supervisor and co-supervisors, and that all scientific publications and other sources used in this thesis have been properly referenced and listed in the Bibliography section. As the author of this thesis, I declare that, to the best of my knowledge, its creation has not infringed upon the copyrights of any third party.

Signed in Prague, 26 April 2024   _____

Acknowledgements

Pyrolýza čistírenského kalu pro sekvestraci uhlíku do půdy

Souhrn

Jednou ze strategií pro zvýšení resilience a kvality zemědělské půdy, snížení dopadů zemědělství na životní prostředí a zmírnění dopadů klimatické změny je sekvestrace uhlíku do půdy – obnova zásob organického uhlíku v půdě. Organická hmota je klíčová pro udržení struktury půdy, pro schopnost zadržovat vodu a pro dostupnost živin. Nicméně snahy o akumulaci organické hmoty v půdě se setkávají s nevyhnutelným dilematem, že cennost a benefity organické hmoty v půdě neplynou pouze z její přítomnosti, ale z jejího rozkladu a průběžné obměny. Pyrolýza organické hmoty na biouhel, též zvaný biochar, je v současnosti propagována jako technické řešení pro zvýšení obsahu uhlíku v půdách, a také jako strategie pro zmírnění změny klimatu prostřednictvím sekvestrace uhlíku do půdy ve formě odolné vůči rozkladu. Výroba biouhlu z čistírenského kalu slouží také jako strategie pro nakládání s tímto odpadem.

Aby byla výroba biouhlu ekonomicky životaschopným podnikáním ve srovnání s materiálovým a energetickým využitím biomasy, organizacemi figurujícími na uhlíkových trzích byly vypracovány metodologie, které činí obsah uhlíku sekvestrovaný v biouhlu obchodovatelný za uhlíkové kredity. Tyto metodologie stojí na modelech rozkladu biouhlu v půdě nebo jeho trvanlivosti ve stavebních materiálech, což poté platí za předcházení vzniku emisí z rozkladu biomasy, přičemž spálení biomasy během procesu pyrolýzy je dle účetního konsensu považováno za uhlíkově neutrální. Uhlíkové kredity jsou nakupovány společnostmi, které tím kompenzují vlastní emise za účelem vytváření marketingových tvrzení o své uhlíkové neutralitě a v jurisdikcích, ve kterých je to povoleno, k plnění stanovených emisních limitů v systému emisních povolenek.

Polní pokus, který je součástí této práce, zkoumá vliv biouhlu vyrobeného z čistírenského kalu a biouhlu ze dřeva na výnosy porostu jílku vytrvalého (*Lolium perenne L.*). V pokusu je také zkoumán vliv přidaných materiálů na obsah uhlíku v půdě s travním porostem a na černém úhoru. Pokus zahrnuje dvě sklizně biomasy během vegetační sezony, analýzu obsahu celkového uhlíku v půdě (C_{TOT}) a oxidovatelného uhlíku (C_{OX}), které jsou obvykle využívány jako ukazatele půdní kvality a průběžně sledovány.

Přidání biouhlu do půdy v první vegetační sezoně nevedlo k průkazným změnám ve výnosu biomasy jílku, tedy nebyl změřen statisticky významný rozdíl mezi výnosy na parcelkách s biouhlem z čistírenského kalu a s biouhlem ze dřeva oproti kontrole. Přidání biouhlu v obou případech vedlo ke zvýšení obsahu uhlíku v půdě, které bylo detekovatelné po vegetační sezoně, ale rozlišení uhlíku z biouhlu a kvantifikace jeho degradace a efektu na původní organickou hmotu v půdě je při analýze půdy náročné. Zda sekvestrace uhlíku v podobě biouhlu představuje také klimatický benefit vyžaduje srovnání s dalším možným využitím zdrojů a energie spotřebovanými pro jeho výrobu a posouzení jeho environmentálních dopadů a benefitů, včetně analýzy životního cyklu celého technologického procesu.

Klíčová slova: biouhel; čistírenský kal; uhlíkové kompenzace; uhlíkové kredity

Pyrolysis of Sewage Sludge as a Method of Carbon Sequestration into Soil

Summary

One of the strategies to improve soil quality and resilience, lessen the effects of land use on the environment, and help mitigate climate change is soil carbon sequestration - rebuilding the reserves of soil organic carbon in croplands. Organic matter is key for retaining soil structure, water-holding capacity, and nutrient availability. However, the efforts to accumulate organic matter encounter an inevitable dilemma that the benefits of organic matter arise not only from its presence, but from its decay and continual turnover in soils. Pyrolysis of organic matter into biochar is currently being promoted as a technical fix for increasing the content of organic carbon in soils and as a strategy for mitigating climate change by carbon sequestration into soils in a form resistant to decomposition. Pyrolysis of sewage sludge into biochar also serves as a waste disposal strategy.

In order to make biochar production an economically viable enterprise compared to demand for materials and energy use of biomass, methodologies have been devised by organizations, which make the carbon sequestered in biochar tradable for carbon credits on carbon markets. These methodologies use decay models to estimate the permanence of biochar in soil or in construction materials, which is then counted as avoidance of future emissions from biomass decomposition, and the biomass combustion during the process is assumed to be carbon neutral, as is the accounting consensus. Companies purchase carbon credits to offset their emissions, allowing them to make marketing claims of carbon neutrality and, in jurisdictions where permissible, to meet the imposed emission limits in emission trading systems.

The field experiment included in this thesis studies the effect of sewage sludge biochar and wood biochar on the growth of perennial ryegrass (*Lolium perenne L.*), and studies the effect of the soil amendments on the soil carbon content under vegetation and on bare fallow. The methodology of the experiment includes two separate harvests during the vegetation season and an analysis of soil total carbon content (C_{TOT}) and oxidizable carbon (C_{OX}), which usually serve as indicators of soil quality and are tracked over time.

According to the results of the field experiment, biochar amendments did not lead to significant changes in biomass yields and there was no significant difference between the yields on plots with sewage sludge biochar and wood biochar. Biochar amendments did lead to increases in soil carbon content detectable after the vegetation season; however, the distinction of biochar carbon content, quantification of its degradation, or its effect on the native soil carbon content is challenging in soil analysis. To determine whether carbon sequestration in biochar also represents a climate benefit requires a comparison with alternative uses of the resources and energy used for its production, an assessment of environmental impacts and benefits, and a life-cycle assessment of the whole technology process.

Keywords: biochar; biosolids; carbon offsets; carbon credits

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1 Introduction

Agricultural land covers around 40 % of the global land surface (Foley et al. 2005). Agricultural systems modify or replace natural ecosystems, and their maintenance requires inputs of energy and materials in the form of synthetic fertilizers, pesticides, irrigation, and fossil fuels powering the machinery. While these inputs have helped meet the essential need for food and materials of the growing and increasingly affluent population, they have also led to widespread degradation of soil, pollution of the environment, and loss of biodiversity. With the prospects of future increase in demand for food and other agricultural products, and climate change threatening food security, the main challenge is to meet the increasing demand for agricultural products, to improve the resilience of agroecosystems to the impacts of climate change, while, at the same time, reducing the negative impacts on ecosystems, human health, and the climate (Tilman et al. 2002; Foley et al. 2005; Campbell et al. 2017).

Due to the inextricable link between C and energy flows through ecosystems, and the role of CO_2 as the primary anthropogenic greenhouse gas, tracking CO_2 emissions and changes of C stocks has become a proxy indicator for the environmental and climate impacts of various human activities (Falkowski 2000; Kleidon 2023). In agricultural systems, soil organic carbon (SOC) and other C indicators are frequently measured to assess soil quality, soil health, and the C dynamics in response to land management practices and environmental conditions (Lal 2016; Liptzin et al. 2022). Soil quality is linked to soil functions in relation to productivity and ecosystem services, whereas soil health emphasizes the role of soil as a living ecosystem with a capacity to sustain biological productivity and environmental quality, and to promote plant, animal, and human health (Lal 2016). Besides various organic fertilizers (manure, compost, biosolids), biochar produced from various biomass feedstocks is also promoted as a strategy to increase the stocks of SOC in a form more resistant to degradation under changing land management practices and environmental conditions (Lehmann 2007).

In contrast to charcoal production or to modern biofuel production which optimizes pyrolysis parameters to produce liquid or gas fractions (Yaman 2004; Devi et al. 2020), the primary aim of biochar production is to avoid the decomposition of the original biomass and, subsequently, to avoid the combustion of the material by its incorporation into soil or other materials (Etter et al. 2021; Puro Earth 2022). Biochar is now also recognized as a "negative emission technology" or a method of "carbon dioxide removal", along with afforestation and reforestation, bioenergy with carbon capture and storage (BECCS), and other geoengineering proposals to mitigate climate change (Smith 2016). However, these technologies may have adverse socio-economic and environmental impacts. Large-scale land conversion for bioenergy, biochar or afforestation have been identified by the Intergovernmental Panel on Climate Change (IPCC) as technologies which can increase risks to biodiversity, water and food security, and local livelihoods and rights of Indigenous Peoples, especially if implemented at large scales in places with insecure land tenure. These technologies are put into contrast with reforestation, peatland restoration, improved forest management, soil C sequestration, and other methods which can enhance biodiversity and other ecosystem functions, and thus improve the resilience of C stocks and sinks in changing climate conditions (IPCC 2023).

2 Objectives

The aim of this thesis was to provide an overview of the carbon cycle from an ecosystemic view and to use the same perspective to describe biochar production as a proposed strategy for climate change mitigation. Second aim was to illustrate the gaps between the aspirations of carbon trading as a tool for climate change mitigation and the principles by which they are limited.

The aim of the experiment was to calculate carbon balance of biochar application into soil, and a comparison with an alternative strategy of sewage sludge management.

3 Literature review

3.1 The global C cycle

The global C cycle involves continuous transformations and exchanges of C compounds between the atmosphere, terrestrial ecosystems, oceans, sediments, and rocks. This cycle involves rapid metabolic and physicochemical transformations, as well as processes spanning decades to geologic timescales. About 90 % of all global C is stored in rocks below the Earth's crust where it is a part of the deep C cycle which influences the global climate in the long term through geologic processes (Hazen et al. 2012).

The main active C pools are the oceans, terrestrial ecosystems, and the atmosphere which serves as a medium connecting the C flows between these pools. The rate of change of atmospheric CO_2 depends on the rates of absorption and emission from the oceans and from terrestrial biosphere. Relatively consistent atmospheric CO_2 concentrations oscillating between 180 and 280 ppmv[1] during glacial and interglacial periods suggest strong mutual feedbacks between terrestrial ecosystems and the oceans which constrain the C sink capacity of one another. The C cycle is also coupled with other biogeochemical cycles, such as the water cycle, and the cycles of nutrients and other elements (Falkowski et al. 2000; Chapin et al. 2009).

The oceans contain the largest amount of C (39 000 Gt C)[2], about 50 times the amount in the atmosphere (785 Gt C). To reach equilibrium, the atmosphere exchanges CO_2 rapidly with the water surface by CO_2 dissolution into a weak acid which then enters the carbonate buffering system. More C is dissolved in cold waters and more of it is released in tropical oceans. The exchange amounts to 90 Gt C annually in both directions. The majority of C (38 000 Gt C) is dissolved in the ocean depths where it is isolated from re-equilibration with the atmosphere by a layer of lighter warmer waters on the surface (Falkowski et al. 2000; Janzen 2004).

In terrestrial ecosystems, the atmospheric CO_2 is embedded into organic matter using solar energy via photosynthesis at the rate of about 120 Gt C per year. About half is quickly returned to the atmosphere by autotrophic respiration as a product of plant metabolism. The rest is temporarily stored in various plant tissues for different amount of time. This represents the energy available for the metabolism and growth of heterotrophic organisms in food webs, which gradually dissipate the energy and release CO_2 through respiration. The amount of C in all living biota is about 400-600 Gt C with about 80 % of it in terrestrial vegetation (Bar-On et al. 2018). The distribution of C in global biomass will be described in more detail in chapter 3.2.

The soils are the largest terrestrial reservoir of C with estimates of 2157-2293 Gt C in the top 1 m. This includes an estimated 695-748 Gt C in carbonate minerals and 1462-1548 Gt of SOC, excluding litter layer and charcoal, which is difficult to quantify in methods used for the determination of organic C in soils (Batjes et al 1996).

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[1] ppmv – concentration of gas molecules in parts per million by volume
[2] Gt = billion (10^9) metric tonnes, also expressed in literature as Pg = petagrams (10^{15} g)

3.1.1 Soil carbon pool

Soil organic carbon (SOC)

Soil organic carbon (SOC) is a crucial and highly dynamic component of terrestrial ecosystems and consists of a range of organic compounds of plant, animal, and microbial origin in various stages of decomposition (Batjes et al. 1996; Post & Kwon 2000). The content of organic matter is beneficial through its physical effects on the soil structure and moisture retention, and chemical effects such as ion exchange and buffering. From a biological point of view, the benefits arise from its potential for decomposition, which increases biological activity and nutrient release. Soil structure is also maintained partly by continual turnover of organic matter (Janzen 2006).

The amount of SOC depends on the net primary production (NPP) of vegetation, the allocation of biomass into the aboveground and belowground parts, and the rate of loss by heterotrophic respiration (decomposition). The mean residence time varies from seconds to thousands of years and depends on the interactions between biological, chemical, and physical factors in the soil and in the surrounding environment (Post & Kwon 2000; Lal et al. 2015). The rate of decomposition is mediated mainly by microbial communities and varies in response to spatial heterogeneity and temporal variations in moisture, temperature, influx of organic C, nutrients, and other factors (Lehmann et al. 2020). In turn, the input of organic C through NPP is, among other factors, limited by the rate of microbial decomposition of organic matter supplying plant-available nitrogen (Chapin et al. 2009).

Most of the energy embedded in soil organic matter is used by microbial communities, with only about 10-15 % being used by soil animals and about 5 % oxidized abiotically. The turnover rate of organic matter is prolonged by three possible mechanisms:

(1) selective preservation of organic matter as a molecular property of plant litter and rhizodeposits (primary recalcitrancy), and of microbial products, humic polymers and charred matter (secondary recalcitrancy);

(2) spatial inaccessibility of organic matter to decomposers through the formation of aggregates, intercalation with phyllosilicates, hydrophobicity and encapsulation in organic macromolecules;

(3) molecular interactions between organic matter and metal ions and other mineral particles (Lützow et al. 2006).

The loss of SOC due to land cultivation is a well-known phenomenon. Soils under cultivation contain 25-75 % less SOC than undisturbed soils in natural ecosystems. The losses after land use change are attributed to decreased inputs of organic matter due to crop harvests, losses by erosion, increased rate of mineralization of residues, leaching, salinization, and higher variations in temperature and moisture. Tillage and cyclical drying and rewetting breaks soil aggregates and exposes organo-mineral complexes to decomposers (Post & Kwon 2000; Lal et al. 2015).

Soil inorganic carbon (SIC)

Inorganic C is present in the form of carbonate minerals such as calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$). Carbonate minerals in soil are derived from the parent material (lithogenic origin) or synthesized through a reaction of bicarbonate ions (HCO_3^-) and Ca^{2+} or Mg^{2+} brought with runoff, dust, manure etc. (pedogenic origin). The content of SIC is estimated around 700-1000 Gt C in the top 1 m of soil. The largest amount of soil carbonates is located mainly in arid and semiarid climates, and in soils over calcareous parent material (Batjes 1996; Lal et al. 2015). Calcareous soils account for about 50 % of the Earth's surface and for about 9 billion ha of arable land (Raza et al. 2021).

In natural conditions, SIC has a mean residence time on millennial timescales and its weathering influences the atmospheric CO_2 levels in the long-term. However, changes in vegetation cover, changes of soil water regime via irrigation, and soil acidification caused mainly by nitrogen fertilization and atmospheric deposition result in more rapid and considerable changes of SIC storage and redistribution even in deep layers of soils (Kim et al. 2020).

Carbonates are the most effective buffering system counteracting the acidification of soils. During the process of neutralization, CO_2 is released into the atmosphere, or it is leached downward into the soil as HCO_3^- where it can precipitate into carbonates again, or it may enter groundwater and resurface later. Whether soils and waters function as net C sinks or net C sources of SIC depends on the hydrological, chemical, and physical conditions which influence the equilibrium of carbonates (Kim et al. 2020).

The losses by CO_2 emissions from carbonates due to nitrogen fertilization are estimated at 7,5 mil. t C per year. Cultivated land loses SIC about 10 times faster than undisturbed natural soils, but even natural soils are acidified by the deposition of nitrogen and sulphur. To counteract the acidification of soils and its detrimental effects on soil structure and fertility, acidic soils are regularly limed which results in additional CO_2 emissions of about 273 mil. t C per year with expected increases in the future (Kim et al. 2020; Raza et al. 2021).

Losses of carbonates in the form of CO_2 directly contribute to climate change by increasing atmospheric CO_2 concentration. Carbonate losses also contribute to climate change indirectly by the detrimental effects on plant and soil productivity, and reduced ability to help form stable complexes of soil organic matter. Current efforts to increase the content of SOC can be undermined and negated by the depletion of SIC (Kim et al. 2020; Raza et al. 2021).

3.1.2 Terrestrial biosphere

Terrestrial biosphere includes all natural, semi-natural, and anthropogenic ecosystems on land. Ecosystems have a central role in mediating the global C cycle and the climate as active and adaptive systems. Together with the oceans, terrestrial ecosystems have absorbed about 50 % of anthropogenic CO_2 emissions in addition to the CO_2 in the natural cycle of growth and decay. It is expected that ecosystems will become a more effective C sink with an increasing atmospheric CO_2 concentration through a so-called CO_2 fertilization effect. In C3 plants, the enzymatic activity of the carbon-fixing enzyme rubisco is saturated at 800-1000 ppmv of CO_2. However, in real conditions the increase in NPP is likely to be limited by water and nutrient availability, and changes in the climate patterns (Falkowski et al. 2000; Chapin et al. 2009).

Land use activities have transformed a large proportion of the planet's natural landscapes into agricultural land, highly managed forests, urban centres, and protected recreational lands. Croplands and pastures occupy around 40 % of the ice-free land surface (Foley et al. 2005) which makes them the most extensive form of land-use (Campbell et al. 2017). This amount corresponds to around 15 million km^2 of cropland (12 % of land) and 28 million km^2 of pastures (28 % of land). The expected increase of agricultural land is by another 8 % by the year 2050 (Campbell et al. 2017).

About one-third to one-half of global ecosystem production is appropriated by human activities. Land use practices provide essential resources for human societies, such as food, fiber, materials, and freshwater but, at the same time, some practices contribute to the degradation of ecosystem services upon which these benefits depend (Foley et al. 2005).

Carbon balance

Carbon balance of fluxes from and into an ecosystem can determine whether it acts as a net C sink or net C source in relation to the atmosphere (Chapin et al. 2006). Net ecosystem production (NEP) can be defined as an analogue to net primary production (NPP):

$$NPP = GPP - AR$$
$$NEP = GPP - ER = GPP - AR - HR = NPP - HR$$

where: NPP – net primary production; GPP – gross primary production (photosynthetic C gain); AR – autotrophic respiration; HR – heterotrophic respiration; NEP – net ecosystem production; ER – ecosystem respiration (AR + HR) (Chapin et al. 2009).

This model functions as a global long-term approximation where the annual C storage in soils (0,5 % of NPP) is roughly balanced by the quantity of C transported by rivers into oceans, subsequent release as CO_2 from waters, and uptake by terrestrial ecosystems which leaves the land close to steady state (Chapin et al. 2006).

When this model is applied to a range of ecosystems and different timescales, the accumulation of C in an ecosystem generally does not correspond to NEP = GPP – ER, for example in ecosystems with significant lateral transfers of C and energy (from farms to cities, in rivers, etc.) (Chapin et al. 2006). It is suggested that due to recent rapid changes, the rate and pattern of NPP and decomposition is also likely to differ in response. These processes include changes in climate and altered frequency of extreme events, hydrologic changes, atmospheric CO_2 increases (CO_2 fertilization effect), land cover change, changes in species composition, and element inputs and losses from active biogeochemical cycles (Chapin et al. 2009).

Net ecosystem carbon balance (NECB) (Fig. 1.) was proposed as a term for the net rate of C accumulation in ecosystems in times of rapid change (agricultural expansion, permafrost thawing, changes in fire regime, etc.):

$$NECB = \frac{dC}{dt} = -NEE + F_{CO} + F_{CH_4} + F_{VOC} + F_{DIC} + F_{DOC} + F_{PC}$$

where: NEE – net ecosystem exchange (flux of CO_2 from/to an ecosystem); F_{CO} – net flux of CO (±); F_{CH4} – net flux of CH_4 (±); F_{VOC} – net flux of volatile organic C (±); F_{DIC} – net flux of dissolved inorganic C (±); F_{DOC} – net flux of dissolved organic C (±); F_{PC} – net flux of particulate (nondissolved, nongaseous) C (±). Particulate C includes for example animal movement, soot emission during fires, deposition and erosion by water and wind, and anthropogenic transport or harvest (Chapin et al. 2006; Chapin et al. 2009).
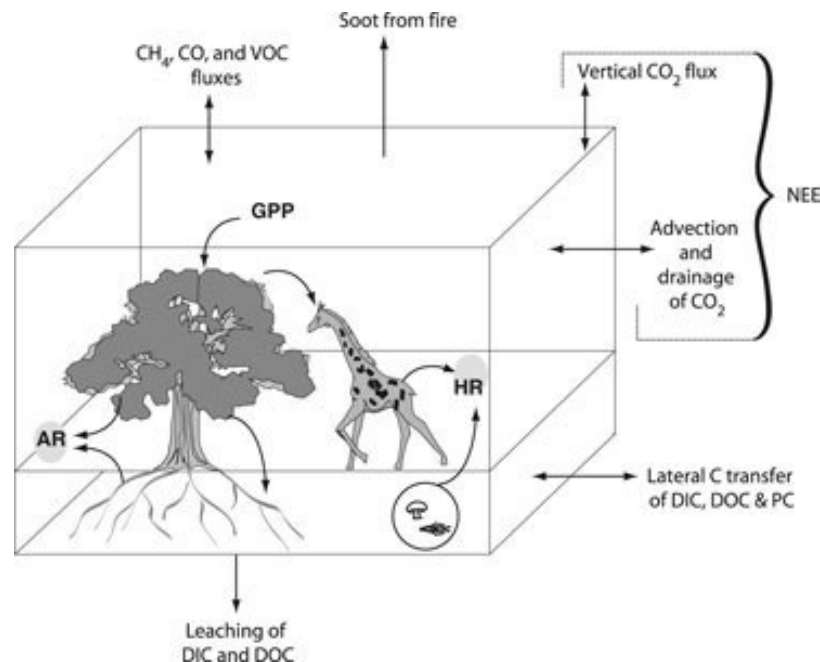
Figure 1. Fluxes of C in the net ecosystem carbon balance (NECB). Source: Chapin et al. 2009.

Climate feedbacks of ecosystems

Besides the ecosystem uptake and release of CO_2 and other greenhouse gasses (CH_4, N_2O) to the atmosphere, other ecosystem changes may have cooling or warming effect on the climate depending on the circumstances and location (Fig. 2.). These climate feedbacks of ecosystems include:

(1) altered albedo (surface reflectivity) which influences the amount of heat which is transferred from the ecosystem into the atmosphere;

(2) altered evaporation from surfaces and transpiration from leaves which transfers heat from the surfaces, increases air moisture which fuels atmospheric mixing, and then releases the latent heat upon water condensation elsewhere;

(3) alterations of longwave radiation which depends on the surface temperature and cloud cover;

(4) changes in production of aerosols which absorb and scatter radiation;

(5) changes in surface roughness which determines the efficiency of water and energy exchange (Chapin et al. 2009).
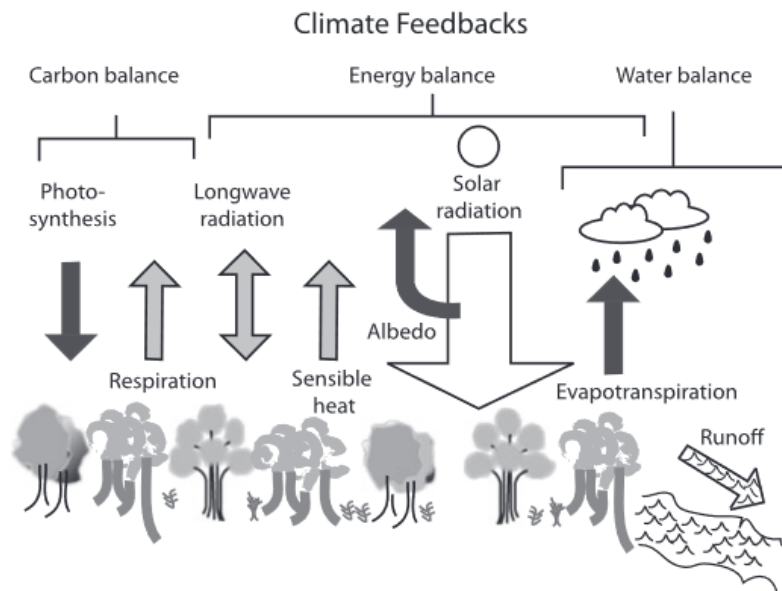

Figure 2. Three major categories of feedbacks between ecosystems and the climate system (carbon balance, energy balance, water balance). Aerosols and surface roughness are not shown. Cooling effects are shown by black arrows, warming effects by grey arrows. Source: Chapin et al. 2009.

3.1.3 Pyrogenic carbon cycle

Wildfires are naturally occurring disturbances which are an important component of the natural C cycle, they reset population dynamics in ecosystems and promote regional biodiversity and heterogeneity (He et al. 2019; Kelly et al. 2020). Exposure to small-scale disturbances builds resilience of ecosystems and their capacity to recover from future disturbances, manifesting as increased stability and productivity over time, if the ecosystem is not pushed too close or beyond a critical threshold (Cabell & Oleofse 2012; Kelly et al. 2020). Many species and ecosystems are adapted to, and depend on, a particular fire regime described by its type, frequency, intensity, and seasonal and spatial distribution. Some species are currently threatened by increased, and some by decreased fire activity. Human induced changes to global ecosystems through land-use change, redistribution of species, and global climate change directly or indirectly interact with fire regimes. More frequent and intensive fires resulting from more intensive droughts are both a consequence, as well as a contributor to acceleration of these changes (Kelly et al. 2020).

Besides CO_2 and other gasses and aerosols emitted during a wildfire, pyrogenic C is formed as a product of incomplete biomass combustion. It is described as a continuum from partly charred biomass, charcoal, condensed graphite, to soot. It is estimated that about 1-5 % of C content in biomass is converted to pyrogenic C during a fire. Due to the formation of

aromatic C structures, pyrogenic C is more resistant to degradation than non-charred biomass, but still, it undergoes physical, chemical, and microbially enhanced degradation. Black C is transported in aerosols, by wind and water erosion from the land surface, and when mixed into soil, it undergoes fragmentation and migrates vertically into deeper soil horizons, groundwater, or nearby waterbodies and soils (Schmidt et al. 2019). Pyrogenic C particles have been also detected in river water, marshes, marine and lake sediments, and in the Arctic where it lowers albedo and induces snow/ice melting (Quinn et al. 2008; Zimmerman & Mitra 2017; Campos & Abrantes 2021).

Though natural phenomena, wildfires have been identified as a major source of environmental contamination by polycyclic aromatic hydrocarbons, along with anthropogenic activities involving combustion (Olivella et al. 2006). Polycyclic aromatic hydrocarbons are an environmental and a health hazard due to their toxicity, mutagenic, carcinogenic and teratogenic potential, high persistence, and tendency to bioaccumulate (Campos & Abrantes 2021).

3.2 Biomass

Global biomass

In life sciences, the term biomass is used for the description and quantification of the mass of living organisms. Biomass in the biosphere is distributed in food chains which can be visualised in trophic pyramids which represent a static picture of the trophic structure of ecosystems – how efficiently energy flows in food webs and how approximately are elements distributed in the biosphere (Bar-On et al. 2018). The combination of conservation of energy and increasing entropy dictated by the first and second laws of thermodynamics requires that the pyramids depicting the biomass production integrated over time have a wider base and narrower top – the primary production is larger compared to herbivores, and the production of herbivores is larger than the production of carnivores (Trebilco et al. 2013).

In pyramids depicting the standing biomass, terrestrial vegetation comprises about 80 % of all biomass (about 450 Gt C). However, in the marine environment, the standing biomass of photoautotrophs (about 1 Gt C) supports a larger standing biomass (about 5 Gt C) of consumers. This can be partially attributed to the rapid turnover of photoautotrophic plankton which in sum has a comparable net primary productivity as terrestrial vegetation (Trebilco et al. 2013; Erb et al. 2018).

The actual biomass of terrestrial vegetation, and of the whole natural biosphere, is currently reduced to about half its potential in the current climate conditions (Erb et al. 2018). Comparison to estimates of prehuman global biomass shows a sevenfold decrease in wild land mammals ($\approx 0{,}02$ Gt C to $\approx 0{,}003$ Gt C), fivefold decrease in wild marine mammals ($\approx 0{,}02$ Gt C to $\approx 0{,}004$ Gt C) but a fourfold increase of the total mammal mass attributed to humans and livestock ($\approx 0{,}04$ Gt C to $\approx 0{,}17$ Gt C) (Bar-On et al. 2018).

Biomass as a resource

In the context of natural resources, the term biomass refers to plant or animal derived materials of recent (non-fossil) origin used for fuel or material production. In this context, biomass is considered a renewable resource and a carbon neutral, or a low-emission substitute

to fossil fuels. The carbon neutrality assumption stems from the IPCC carbon accounting guidelines for emission reporting where emissions from biomass combustion can be reported as a change of C stock in the land-use sector in the country of origin, instead of the energy sector at the point of combustion as a way to avoid double-counting. Several policies endorsing biomass as carbon neutral energy were implemented with asymmetric considerations only for one of these two "pools". The repeated assumption stemming from this policy is that the emissions from biomass will be sequestered sooner or later by plant growth, and its combustion will not result in CO_2 accumulation in the atmosphere (Haberl et al. 2012).

These policies are based on a baseline error in C accounting by failing to recognize the counterfactual scenario: if plants were not harvested for biofuel production, they would continue to absorb CO_2 from the atmosphere. Similarly, if croplands used for biofuel production were allowed to reforest, they would also help reduce atmospheric CO_2 (Haberl et al. 2012). Crops grown for food or biofuel production are not included in the calculations of C stocks in the land-use sector. The assumption here is that the biomass is converted into CO_2 emissions in the same year by consumption or by combustion (Frankelius 2020).

The role of vegetation as a C sink is already counted in the projections of future temperature rise. Counting the same vegetation as carbon-neutral biofuel; therefore, results in another accounting error by double-counting its benefits. If biomass is used as fuel in a scenario where fossil fuels would be used instead, it only leads to less fossil fuels being used, but the contribution to atmospheric CO_2 is similar. Biomass combustion, per unit of energy, typically produces more emissions because it contains less energy per unit of C and is usually burned with a lower efficiency (Haberl et al. 2012).

In the European Union, biomass accounts for about 60 % of renewable energy sources and 10 % of all energy sources. The majority of biomass is sourced from forestry (60 %), agriculture (27 %), and municipal and industrial waste (12 %) (European Commission 2019). It has been estimated that about 45 EJ/yr of global energy is generated from biomass. This includes biomass used as biofuel for heat and electricity generation (6 EJ/yr), and traditional use for cooking and heating (39 EJ/yr). Using different calculation approaches, the potential for future bioenergy scaling has been estimated as 200 EJ/yr, or even 1000 EJ/yr by the year 2050 (Williams et al. 2012).

Biomass varieties used as fuel are divided according to their biological diversity, source, or origin into the following groups:
(1)   Wood and woody biomass: whole stems and branches, foliage and bark, processed wood into chips, pellets, briquettes and sawdust etc.;
(2)   Herbaceous and agricultural biomass: grasses and flowers, straws, processed biomass and other residues (shells, pits, bagasse etc.);
(3)   Aquatic biomass: marine and freshwater algae, seaweed, kelp etc.;
(4)   Animal and human waste biomass: bones, meat-bone meal, chicken litter, manure and faeces etc.;
(5)   Contaminated biomass and industrial biomass wastes: municipal solid wastes, sewage sludge, paper sludge and wastepaper, used wooden products (plywood, pallets, etc.);
(6) Biomass mixtures: mixtures of the above varieties (Vassilev et al. 2010).

3.2.1 Chemical composition of biomass

From a chemical point of view, biomass is a heterogenous mixture of organic and inorganic matter organized into complex structures of solid, fluid, and gaseous phases. The chemical and structural composition of biomass is very diverse and reflects the diversity of its sources – the biomass species, type of tissue, growth stage, environmental factors, and processing steps. For analytical purposes, the chemical components of biomass are grouped as: structural components, extractives, and ash. Contaminated biomass may contain materials of non-biomass origin incorporated during the processing steps (Vassilev et al. 2010, 2012).

The majority of biomass is of plant origin and the bulk is composed of varying proportions of cellulose (40-60 %), hemicellulose (15-30 %) and lignin (10-25 %), the main structural biopolymers in plant cell walls (Wang et al. 2017).

Extractives include a wide range of non-structural compounds which can be extracted from biomass by polar or non-polar solvents. Extractible compounds include mainly proteins, lipids, non-structural carbohydrates, pigments, tannins, resins, and other minor components.

Ash is the residue of complete combustion (oxidation) of biomass and represents an approximation of the inorganic matter in biomass. Inorganic matter includes minerals, semi-crystalline mineraloids and amorphous matter. Ash is composed of the original and newly formed inorganic components from the inorganic, organic, and fluid matter. Depending on the source, the ash yield determined at 550-600 °C varies in the range of 0,1-46 % (mean 6,8 %) on dry basis (Vassilev et al. 2010, 2012). Chemical composition of selected biomass varieties are shown in Tab. 1.

Table 1. Comparison of the average composition of selected biomass varieties. Source: Adapted from Vassilev et al. 2010.

	Proximate analysis (db[a]), % (wt.)			% (wt.) in A[b]	Ultimate analysis (daf[c]), % (wt.)				
	VM[d]	FC[e]	A	P	C	O	H	N	S
Wood biomass	78	18,5	3,5	1,52	52,1	41,2	6,2	0,4	0,08
Herbaceous/agricultural biomass	75,2	19,1	5,7	2,83	49,9	42,6	6,2	1,2	0,15
Sewage sludge	48	5,7	46,3	6,93	50,9	33,4	7,3	6,1	2,33

[a]Dry basis
[b]Ash
[c]Dry ash free basis
[d]Volatile matter
[e]Fixed carbon

3.2.2 Sewage sludge

Sewage sludge is a biodegradable by-product resulting from the municipal or industrial wastewater treatment process. The primary objective of wastewater treatment is sanitation and environmental protection; therefore, the production of sludge is unavoidable. The amount of produced sewage sludge is increasing not only as a consequence of accelerated urbanisation, but also because of increasing requirements on the quality of the water effluent returning to the environment. This requires lengthened retention time and increased growth of the sludge

(Peccia & Westerhoff 2015; Đurđević et al. 2020). In the Czech Republic, about 200 thousand dry tonnes of sewage sludge is produced annually (CZSO 2022). In the EU, the amount produced is estimated at 13 million dry tonnes annually (Samolada & Zabaniotou 2014). The management and disposal of sewage sludge is also an environmental issue and an economic burden. The sludge treatment costs may reach 20-60 % of the total operating costs of the wastewater treatment plant. Sludge represents only 1-2 % of the total volume of wastewater (Đurđević et al. 2020) and the reduction of sludge volume and the pathogen load are the primary objectives before the sludge can be transported off site. After this stage, the dewatered and digested sludge contains approximately 15-30 % of dry solids and is often euphemistically labelled as "biosolids" and it is then transported for reuse or disposal (Wang et al. 2008).

Methods of disposal and reuse

With regard to the principles of circular economy which prioritizes the reuse and material recovery from waste, the application of biosolids in agriculture would be an optimum solution due to the content of valuable organic matter, nitrogen, phosphorus and micronutrients, and its positive effect on soil texture and water-holding capacity (Domini et al. 2022). The reuse of biosolids on agricultural land is regulated due to the content of heavy metals, pathogens, and other pollutants which may harm the environment and enter the food chain. It is also limited by negative public image and the availability of agricultural land in the region (Peccia & Westerhoff 2015; Domini et al. 2022). Composting of sewage sludge before land application may be an option for reducing the content of some contaminants and pathogens (Lü et al. 2021).

Other pathways include thermal treatment with energy recovery. Organic matter in the sewage sludge contains energy in the order of 15-20 MJ/kg on dry matter which can be partially utilized by anaerobic digestion. Anaerobic digestion combines the advantage of biogas production and hygienization of the sludge before further use (Peccia & Westerhoff 2015). Biogas usually contains 55-75 % CH_4, 25-45 % CO_2, N_2, H_2, H_2S and O_2 (Demirbas et al. 2016) and it can be used on site for electricity and heat cogeneration to cover the energy needs of the wastewater treatment plant. Alternatively, it can be upgraded to biomethane and sent to the grid or compressed and used as transportation fuel (CNG) (Peccia & Westerhoff 2015). The remaining stabilized sludge (biosolids) has lower biodegradability, and it still contains energy in the order of 9-13 MJ/kg in dry matter. Its further application should primarily aim at its reuse, material recovery or energy use (Domini et al. 2022).

Energy can be recovered by mono-incineration or co-incineration of sludge, ideally with subsequent ash processing for the extraction of phosphorus and other resources. For this purpose, mono-incineration is more suitable (Hušek et al. 2022). Alternative but only small-scale thermal treatment methods include pyrolysis, gasification, and hydrothermal liquefaction (HTL) which are driven by biofuel research and attempts to extract energy and nutrients from waste streams (Peccia & Westerhoff 2015). Pyrolysis and gasification are also driven by an interest in negative emission technologies (Renner 2007; Schmidt et al. 2019; Brown 2021). Suitable applications and the potential benefits and trade-offs of these methods in comparison to incineration are being studied (Hušek et al. 2022).

Disposal on landfills is the least preferred option because it represents a material and energy loss, and an environmental burden. Landfilling of biodegradable waste in the EU should gradually phase out (Collivignarelli et al. 2019).

3.3 Pyrolysis of biomass

Pyrolysis is defined as chemical decomposition (cleavage of chemical bonds) induced only by exposure to a high temperature in an inert environment (Alemán et al. 2007). Temperature during pyrolysis of organic compounds is typically between 300 °C and 800 °C which differentiates the process from thermal degradation or natural chemical decomposition in lower or even in ambient temperature. The necessity of inert atmosphere differentiates pyrolysis from combustion which requires oxygen for the ignition and oxidization of the feedstock. Anoxic conditions are commonly achieved by the flow of inert gasses (N_2, He, Ar), or reductive gasses (H_2, CH_4, NH_4), or vacuum inside the reactor. Thermal dissociation of chemical bonds in the material prevails during pyrolysis but partial bond formation and rearrangement also takes place. Oxygen and residual moisture content within the feedstock may lead to reactions comparable to partial combustion or gasification (Van De Velden et al. 2010; Devi et al. 2020).

The resulting products of pyrolysis are a combination of solid, liquid, and non-condensable gas fractions, all of which contain a large number of product species. The composition of these fractions and their proportion in the final result are highly variable and depend on the feedstock composition, particle size, and the pyrolysis parameters. These parameters include temperature, heating rate, residence time of vapour, pressure, atmosphere composition, and the reactor design (Sharma et al. 2015; Wang et al. 2017).

Due to the chemical and structural heterogeneity of biomass and many variables in the pyrolysis parameters, the reaction kinetics cannot be accurately described by a sequence of reactions with respective activation energies. Rather, a series of parallel and concurrent reactions takes place with varying distribution within individual particles and through the whole sample. The main challenge is the optimization of the pyrolysis parameters for a particular feedstock in order to obtain the desired products (White et al 2011; Devi et al. 2020). A number of mathematical models of varying complexity are being devised for this purpose (Sharma et al. 2015).

One of the most widely studied applications of pyrolysis is the production of biofuels and waste valorisation. The main focus of modern pyrolysis is the production of liquid bio-oil and its upgrading to liquid fuels and chemicals with more versatility than solid biofuels (Fonts et al. 2009; Van De Velden et al. 2010). For this purpose, the pyrolysis parameters are optimized to maximize the yield of the liquid or gas fractions, and the charred residue can be considered a by-product which can be burned as fuel to power the process or to dry the feedstock (Sohi et al. 2010). Pyrolysis is, and traditionally has been, also used for production of charcoal or activated carbon (Devi et al. 2020). This charred material is also called biochar when it is produced for the purpose of carbon sequestration (Lehmann et al. 2006; Gaunt & Lehmann 2008).

3.3.1 Primary reactions

Pyrolysis of biomass is often simplified into the description of conversion mechanisms of the main biopolymer constituents. The primary mechanisms leading to the final pyrolysis products are: fragmentation, depolymerization, and char formation. During these reactions, chemical bonds are broken, rearranged, and volatile compounds are released.

Char is the solid residue consisting mainly of aromatic polycyclic structures. Its formation is generally the result of rearrangement reactions within and between molecules which form benzene rings combined into polycyclic structures.

During depolymerization, the biopolymers which are the main constituents of biomass are broken down into shorter chains until the molecules become volatile. These molecules are condensable at ambient temperature and are found in the liquid fraction as monomers, dimers, and trimers.

Fragmentation reactions result in a wide array of incondensable and condensable molecules by linking and fracturing covalent bonds within the monomer units and within the polymer (Collard & Blin 2014).

3.3.2 Secondary reactions

Before the volatile compounds released from the sample can be carried away by the flow of gas, they may undergo secondary reactions on surfaces inside the biomass particles or on surfaces of the sample and the reactor. The occurrence of these reactions is usually not desirable, and they are more likely to occur if the residence time of volatiles in the reactor is long. These reactions include cracking and recombination (Collard & Blin 2014). Neves et al. (2011) give a longer list of secondary reactions where they include cracking, reforming, dehydration, condensation, polymerization, oxidation and gasification, and water-gas shift.

Cracking reactions of volatiles result in the formation of molecules of lower molecular weight, leading to an increase of the yield of non-condensable gasses at the expense of the yield of liquids. Chemically, the products of cracking are similar to products of primary fragmentation, the difference is in the pathway of formation. Cracking reactions were shown to have a significant effect on the final products at pyrolysis temperatures above 600 °C (Van De Velden et al. 2010; Collard & Blin 2014).

Recombination reactions occur at pyrolysis temperatures over 800 °C and leads to formation of molecules of higher molecular weight which may result in the formation of secondary char inside the particle pores. In the gas phase, recombination may result in increased concentrations of polyaromatic hydrocarbons (PAH) (Collard & Blin 2014).

3.4 Biochar

Biochar is a porous C material similar to charcoal or char which are terms for the solid C residues obtained by pyrolysis or by incomplete combustion of organic material. Their C content comprises mainly of polyaromatic structures in irregular arrangements with some content of oxygen, hydrogen, nitrogen, and ashes (Lehmann & Joseph 2009). The term biochar, or bio-char, was coined in 2005 by Peter Read, a specialist in energy economics (Read 2009), and Johannes Lehmann, a soil scientist, and his coworkers who established it as a material produced for the purpose of permanent C sequestration with a view of its valorisation via C trading mechanisms which were emerging at that time. The difference between biochar and other forms of pyrogenic C is, therefore, not in the feedstock or in the method of production, but in the purpose for its production (Lehmann et al. 2006; Lehmann & Joseph 2009; Sohi et al. 2010).

Before the concept of biochar was established, the use of charcoal as a C sink was suggested by Seifritz (1993) who proposed that industrialized countries compensate for their greenhouse gas emissions by paying developing countries, mainly in South America, for continual production of charcoal and making an agreement not to burn it. This charcoal is then to be stored in dedicated valleys or artificial mountains and covered or gradually layered by soil. This line of thinking is based on the idea that once trees on plantations grow into an appropriate size and capture enough CO_2, they need to be safely and permanently disposed of in the form of charcoal, in order to avoid their decomposition. The estimate here is that 60 % of C in the wood is turned into charcoal and 40 % is burned during the process for heat generation. An estimated requirement for a theoretical 1 MW coal-fired power plant with a mean annual load of 0,8 would be an area of 1130 ha of poplar trees which would be harvested and turned into charcoal every 15-25 years, without counting the 40 % of C emitted from the biomass combustion. As of 2022, the total capacity of coal-fired power plants was 2 082 581 MW (Global Energy Monitor et al. 2023).

Biochar production is based on a similar concept, except that it differs in the proposed range of possible biomass feedstocks and the main method of disposal – the incorporation into soils of terrestrial ecosystems, mainly croplands and grasslands. The incorporation into construction materials or filters was also considered as a C sink early on (Okimori et al. 2003; Lehmann et al. 2006). The potential biochar applications have since expanded to include electronics, animal feed additive and manure treatment in agriculture, compost additive, additive to planting substrate, substrate for green infrastructure in cities, soil remediation, soil amendment, and nutrient carrier in fertilizing products (Schmidt et al. 2019; Novotný et al. 2023; Wang et al. 2023). Biochar primarily is not produced to serve as fertilizer, though it may retain a portion of nutrients from the original biomass bound in some form (Cao & Pawlowski 2013; Lehmann & Joseph 2009).

As a thought experiment, several C sequestration variants have been explored using the same C accounting approach as for biochar, such as: injection of pyrolytic gas into geologic storage, injection of pyrolysis oil into old oil wells or its incorporation into asphalt (Schmidt et al. 2019). Related ideas which have been proposed include direct wood burial (Zeng 2008), disposal of crop residues into deep ocean beds (Metzger & Benford 2001) or storage of salted biomass in dry landfills (Yablontovitch & Deckman 2023).

The narrative which serves for spreading the interest in biochar is the connection to dark anthropogenic soils found in the Amazon region, the Terra Preta soils, which show higher fertility and higher proportions of black C than soils on adjacent plots (Sohi et al. 2010; Lehmann & Rondon 2006). These soils were formed over hundreds and thousands of years by indigenous populations and there are multiple reasons for their increased fertility. It is however being associated mainly with the content of black C from kitchen fires, field burning or deliberate application, which gives these soils a typical black colour (Lehmann & Rondon 2006; Lehmann 2007; Sohi et al. 2010). This connection has an appeal as a rediscovery of ancient indigenous wisdom (Lehmann & Joseph 2009), however, in a report by the Expert Group for Technical Advice on Organic Production of the European Commission (EGTOP) it has been emphasized that this association is misleading (EGTOP 2022).

The main opportunities where biomass could be sourced for the purpose of biochar production were initially identified as:

(1)   tropical ecosystems where shifting slash-and-burn method of cultivation would be replaced by slash-and-char cultivation;
(2)   burying unused charcoal from charcoal production in developing countries;
(3)   agricultural residues and forest residues, such as logging residues, decaying wood, crop residues, and manure;
(4)   biochar produced by already existing biofuel industry using energy crops and residues;
(5)   dedicated plantations for biochar production or for a joint biofuel and biochar production (Lehmann et al. 2006; Lehmann & Joseph 2009).

Industrial and municipal residues or sewage sludge were not included in the initial considerations for biochar production due to the potential for environmental contamination by organic pollutants and heavy metals (Lehmann et al. 2006). Rumphorst and Ringel (1994) saw the benefits of sewage sludge coke (char) mainly in its reduced volume compared to sludge and reduced content and mobility of pollutants, mainly with a view of better suitability for landfilling. Other proposed uses were as neutralizer in already existing sewage sludge landfills, adsorptive medium in gas purification or as growth surface in biological purification stage in the wastewater treatment plant.

Pyrolysis and biochar production are used and further researched in the context of climate change mitigation, biofuel production, agriculture, pollution control, and waste management. It is therefore suggested that biochar production should be partnered with wastewater treatment plants, as well as food processing industry and any locally specific sources of biological waste (Sohi et al. 2010; Lehmann 2021).

Using different approaches to calculate the amount of available biomass, it was estimated that biochar production could be used to offset 10 % of annual emissions from fossil fuels in the US from domestic sources (Lehmann 2007), 12 % of global anthropogenic emissions annually (Woolf et al. 2010) or 6 % of GHG emissions from selected countries over a 100-year period (Lefebvre et al. 2023). Current efforts of biochar proponents revolve around influencing public perception, policy, and regulation to allow the scaling up of the industry, and developing carbon markets as a source of finance (Lehmann 2021; IBI 2022).

3.4.1   Environmental persistence

The C sequestration potential of biochar is based on its resistance to decomposition. The withdrawal and conversion of biomass into biochar is considered a net removal of CO_2 from the atmosphere and counted as avoidance of emissions arising from future decomposition of biomass. When biochar is transferred into soil, it is then considered as a more secure and unlimited method of increasing the "stocks" of SOC than relying on perpetually maintained land management practices which increase the equilibrium level of SOC (Lehmann 2007; Sohi et al. 2010).

Biochar in soil is more stable than uncharred organic matter, however, it still undergoes biotic and abiotic oxidation, as well as physical disintegration into micro- and nanoparticles which are then transported into deeper soil layers and sediments of rivers, lakes, and seas (Lehmann et al. 2006; Schmidt et al. 2019).

The estimates of biochar persistence vary widely, from single years to millennial timescales. The persistence of biochar depends primarily on the environmental conditions and the properties of biochar, largely determined by the type of feedstock and pyrolysis parameters. Due to a lack of long-term field experiments, the stability of biochar is extrapolated from annual or decadal field studies, natural wildfires, archaeological findings, or laboratory incubation studies. Difficulties arise due to the number of possible variations of biochar properties and experimental conditions, different assumptions around the age, sources and input quantities of charred matter found in nature, quantification of biochar mineralization separately from other sources of CO_2, and the quantification of physical losses by erosion or leaching through the soil profile (Lehmann et al. 2009; Budai et al. 2013).

Environmental conditions which have been shown to influence the persistence of biochar include temperature and moisture regime, soil type, texture, pH and mineralogy, tillage, additional organic matter inputs, and vegetation fires (Lehmann et al. 2009).

Regarding the influence of biochar properties on its persistence, pyrolysis temperature and molar H/C_{org} and O/C_{org} ratios of biochar elemental composition are used as proxy indicators for the degree of condensation – the formation of aromatic structures at the expense of H-C bonds and organically bound oxygen (in biomass with low ash content). Higher pyrolysis temperature and lower H/C_{org} and O/C_{org} ratios are related to longer environmental persistence (Woolf et al. 2021).

3.4.2   Effects on soil

In methodologies used by companies certifying carbon credits, a proof is required that the end use of biochar was other than energy use, for example, as an addition into greenhouse substrate, soil additive, animal feed additive, water treatment, insulation, landfill/mine absorber or cement/asphalt addition (Etter et al. 2021; Puro.Earth 2022). The function of soil in the context of C sequestration is to serve as storage for biochar (Lehmann et al. 2006) and as an insurance against its energy use (Etter et al. 2021; Puro.Earth 2022). Compared to other applications, the reasons behind the propositions for biochar incorporation into agricultural soil are mainly the following:

(1)   the potential capacity for long-term biochar storage in the estimated amounts relevant to the scale of anthropogenic greenhouse gas emissions;

(2) potential improvement of productivity to offset the energy value lost in biochar;

(3) possible suppression of CH_4 and N_2O emissions from soil, and the effects on intrinsic organic C as secondary climate benefits (Sohi et al. 2010).

It was acknowledged that the maximalization of the amount of biochar added to soil for climate change mitigation and revenues from carbon credits may not be compatible with benefits to soil, plants grown on it, and the wider environment (Lehmann et al. 2006). It was hypothesized that biochar application into soils can be beneficial for plant growth up to a certain concentration, depending on the properties of biochar, soil properties, other additions of nutrients and organic matter, and the crop species (Lehmann & Rondon 2006).

Based on a greenhouse pot experiment growing cowpea in Ferrasol with a maximum biochar dose equivalent to 135,2 t C/ha (Lehmann et al. 2003), the potential maximum capacity of global croplands (1,6 billion ha) and temperate grasslands (1,25 billion ha) was estimated as 224 Gt C and 175 Gt C, respectively, using a rounded-up biochar dose equivalent to 140 t C/ha (Lehmann et al. 2006).

Improved crop productivity can be attributed to biochar additions already at low application rates (0,4–0,8 t C/ha) compared to control with no soil amendment. This can be a result of direct addition of nutrients brought in biochar and greater nutrient retention (Lehmann & Rondon 2006). Increases in yields have also been attributed to increased water-holding capacity of soil (Schimmelpfennig et al. 2014).

Studies assessing the ecotoxicity of biochar to soil invertebrates, such as earthworms, springtails, and ants, have shown some negative and some positive or neutral responses (Brtnicky et al. 2021). The variety of observed biological responses to biochar addition could be explained by several factors:

(1) low palatability and nutrition value, though a potential source of energy;

(2) biochar pores serving as habitat for some microorganisms and in turn as a source for microbial grazers;

(3) pollutant content in biochar harming soil biota (heavy metals, PAHs);

(4) change of abiotic conditions (pH, water availability) beneficial or harmful to different organisms (Briones et al. 2020).

Regarding the content of PAHs in biochar, the Council Regulation (EU) 2019/1009 sets the limit of "16 priority PAHs" in biochar used as a fertilising product at 6 mg/kg on dry matter. A concern has been raised by EGTOP that standard analytical methods may be underestimating the amounts of PAHs brought into the soil in some biochar materials due to their sorption to the char surface, and the authorization of biochar for use in organic agriculture is to be re-evaluated (EGTOP 2022).

3.4.3 Carbon accounting methodologies

For consistency with current climate policies, the C accounting methodologies calculate the fraction of biochar C remaining in soil after 100 years. These calculations require data on the mass of biochar, its organic C content, and a decay model for the estimation of a factor of permanence calculated for a 100-year period. These models are based on the pyrolysis temperature and the properties of biochar, such as the molar ratio of hydrogen and organic C content (H/C_{org} ratio) and are then adjusted for an average ambient temperature or average soil temperature (IPCC 2019; Woolf et al. 2021).

In the 2019 refinement of C accounting guidelines, the IPCC (2019) provided a basic method for estimating the changes of organic C from biochar amendments in mineral soils to be used by countries in their National Greenhouse Gas Inventories:

$$\Delta BC_{mineral} = \sum_{p=1}^{n} (BC_{TOT} \cdot F_{C_p} \cdot F_{perm_p})$$

$\Delta BC_{mineral}$ – the total annual change of biochar organic C stock in soil (t/year);
BC_{TOT} – the total amount of biochar added in dry matter (t/year);
F_{C_p} – the fraction of organic C content in biochar for each production type;
F_{permp} – the fraction of biochar organic C remaining after 100 years.

Due to the persistence of biochar, the changes in soil organic C from biochar amendments must be estimated separately from other organic amendments and management practices which are estimated by a stock change method and tracked over time. The values for F_{permp} are calculated for three intervals of pyrolysis temperature and for naturally occurring chars of unknown origin (Tab. 2.). The values are based on available data from field and laboratory studies exceeding a one-year duration. Values are then adjusted for an average annual temperature of 20 °C to provide some safety margin. Because this method is considered only a basis for future development, specific measurements of biochar properties (H/C_{org} and O/C_{org} ratios), soil properties, temperatures, and moisture regimes are not considered (IPCC 2019).

Table 2. Values for F_{perm_p} (fraction of biochar organic C remaining in soil after 100 years). Source: Adapted from IPCC (2019).

Production	Values for F_{perm_p}*
High temperature pyrolysis and gasification (> 600 °C)	0,89 ± 13 %
Medium temperature pyrolysis (450-600 °C)	0,80 ± 11 %
Low temperature pyrolysis (350-450 °C)	0,65 ± 15 %
Unknown origin	0,56

*mean value ± 95 % bootstrap confidence interval

Woolf et al. (2021) have rewritten the IPCC equation to directly recalculate the organic C content into an equivalent of avoided CO_2 emissions and have also included an optional method for the estimation of avoided N_2O emissions from soil to count as additional climate benefit as follows:

$$GHG_{bc} = M_{BC} \cdot F_C \cdot F_{perm} \cdot {}^{44}/_{12} + 0{,}23 \cdot n \cdot GWP_{N_2O}$$

GHG_{bc} – net avoided emissions by biochar (CO_2e);
M_{BC} – total amount of biochar added to soil (t);
F_C – fraction of organic C in biochar on dry matter basis;
F_{perm} – fraction of biochar organic C remaining after 100 years;
44/12 – molar conversion factor from C to CO_2e;
$0{,}23 \cdot n$ – 23% avoidance of locally specific annual N_2O emissions;
GWP_{N2O} – the most recent value of global warming potential of N_2O given by the IPCC.

In a similar fashion as in the IPCC method, the values for F_{perm} are modelled as a function of pyrolysis temperature and additionally as a function of the molar H/C_{org} ratio of biochar. In the provided model, the values can be recalculated for any soil temperature for time periods ranging from 100 to 1000 years. But still, the method does not take into account any local environmental specifics and soil properties besides average soil temperature, and its easy applicability is a trade-off to its accuracy (Woolf et al. 2021). Additionally, inputs of low H/C_{org} ratio and low soil temperatures produce F_{perm} values exceeding 100 % – more carbon remaining in soil than was applied. The values are simply corrected to 100 % when the model is used for calculation of carbon credits (Puro Earth 2022).

3.4.4 Life Cycle Assessment

Life Cycle Assessment (LCA) is an ISO standardized method which is used by companies and in theoretical studies for the evaluation of the potential environmental impacts of products or technological processes. Life Cycle Assessment studies should include all life stages from the acquisition of raw materials, production of intermediate and final products, the use phase, and the recycling and disposal. Along with a series of GHG Protocols, it is one of the tools used for GHG emission accounting and reporting, each with specific requirements, guidelines, and possible interpretations (Matuštík et al. 2022; Weidema 2022).

Life Cycle Assessment is being increasingly used to assess biochar production and its potential benefits in climate change mitigation. It is performed on a case-by-case basis and its results relate only to a specific production process using specific feedstock in a specific location. The benefit of LCA is that it makes use of real-life data and an extensive database of data provided with the accounting software. However, the scope of the analysis is unavoidably limited and provides a more or less linear picture of a complex system (Matuštík et al. 2020). When defining the system boundaries, decisions must be made concerning the boundary between the natural environment and the technical system, boundaries between upstream and downstream technical systems, and the cut-off criteria for deciding between significant or insignificant side streams (Yoshida et al. 2013). There are many combinations of production circumstances, system boundaries, and methodological decisions which are allowable within

the LCA standard. Comparison of various production pathways is possible only if the system boundaries and methodologies are identical (Pradel et al. 2016; Matuštík et al. 2020).

One of the most controversial issues in C accounting is how greenhouse gas emissions from "biogenic" C are treated – whether the emissions from biomass are included or excluded. Carbon neutrality of biomass combustion is the baseline assumption in most LCA studies. The basic idea is that the CO_2 captured by plants would re-enter the atmosphere sooner or later, similarly as are the assumptions around the inherent C neutrality of biofuels. Following this are proposals that LCA should give credit to the emission delay (C sequestration) in wood products and other bio-based products, compared to biofuels (Vogtländer et al. 2014; Matuštík et al. 2022).

Life Cycle Assessment of biochar production

Biochar production requires sufficient supply of biomass which needs to be obtained, or grown and harvested, transported, and processed. The system also requires an input of energy and material for the construction, operation, and maintenance of the pyrolysis plant, and for the transport and soil application of biochar. The combustion of pyrolytic oil and gas can be used for electricity and heat cogeneration to cover the internal energy consumption, or it can be sold as additional product (Matuštík et al. 2022). In biofuel production, pyrolysis can be optimized to maximize the yield of pyrolysis oil or gas, and the residual char is burned as fuel during the process (Devi et al. 2020).

Despite pyrolysis being an industrial process, biochar is considered a "negative-emission technology" and a method of soil C sequestration leading to net avoided emissions as a basis of its climate benefit. As was demonstrated by Matuštík et al. (2022) in a case study of biochar produced in a gasification plant in Zlatá Olešnice (the biochar used in our experiment), methodological decisions in the LCA can change the whole perception of a technology process. The facility in Zlatá Olešnice produces biochar from used wooden pallets. The LCA study compares the gasification process to waste incineration or landfilling. When emissions from biomass were not considered, as is the consensus, the gasification system appeared beneficial to climate in every scenario. When the emissions from biomass were included, the system became a climate change contributor in most scenarios. The result was mainly influenced by the energy source being replaced by the produced gas. Additional important factor was transport distance.

As a waste disposal strategy, gasification of biomass appears favourable compared to other pathways. However, this conclusion requires the assumption that wooden pallets are a waste which cannot be reused or recycled (Matuštík et al. 2022). Similar LCA studies of biochar production calculating its climate benefit require the assumption that any biomass used as feedstock is a waste with no potential for reuse or recycling (Smebye et al. 2017; Matuštík et al. 2020).

3.5 The Paris Agreement

In 2015, the Paris Agreement introduced an ambition to achieve a goal of net-zero anthropogenic emissions by 2050. Net-zero is defined as a balance between anthropogenic emissions by sources and removals by sinks of greenhouse gasses. The goal is to keep the rise of the global mean temperature well below 2 °C and, if possible, below 1,5 °C compared to pre-industrial era (Schleussner et al. 2016; UNFCCC 2016). This goal is principally based on the Assessment Reports by the IPCC which provide a scientific basis for political decisions concerning climate change. The IPCC creates models of possible emission pathways to different peak warming levels, makes predictions of the impacts, risks, and vulnerabilities, and then outlines the possible actions to achieve formally agreed goals (Schleussner et al. 2016; IPCC 2018).

The framing of climate goals in terms of the global mean temperature has led to the development of the concept of global C budget, representing the cumulative anthropogenic emissions since the start of the industrial era and the remaining "allowable" emissions (Lawrence & Schäfer 2019). Estimates by Friedlingstein et al. (2022) of the remaining C budget are 105 Gt C (380 Gt CO_2) and 335 Gt C (1230 Gt CO_2) for a 50 % chance to meet the respective targets of 1,5 °C and 2 °C by the year 2100. Assuming the 2022 annual emissions level of 11,1 Gt C (40,5 Gt CO_2), this would leave 9 and 30 years for the respective targets.

Nationally determined contributions (NDCs)

The Paris Agreement works with the legal principle of "common but differentiated responsibilities", referring to shared obligations but unequal distribution of historical responsibility for climate change among countries (UNFCCC 2016). To date, the Paris Agreement has been signed by 195 countries and all are required to formulate their own mitigation targets, called Nationally Determined Contributions (NDCs), based on their individual capabilities and national circumstances. The requirement is that countries submit their NDCs and raise their individual targets every five years. The progression should "reflect the highest possible ambition" and lead to economy-wide coverage of emissions and eventually to net-zero (Schleussner et al. 2016; UNFCCC 2016; Ahonen et al. 2022). Most participating countries are planning to achieve net-zero between 2050 and 2060 (Chen et al. 2022).

Full implementation of all national commitments is estimated to result in a 5,3 (2,3-8,2) % emission reduction by 2030, relative to 2019 levels. The IPCC scenarios for the same timeframe require emission reduction of 43 (34-90) % and 27 (13-45) % for the respective targets of 2 °C and 1,5 °C. In terms of the carbon budget, estimated 87 % and 38 % of the budget for the respective targets will be spent by 2030 (UNFCCC 2023).

3.6 Carbon markets

Carbon markets have become one of the most favoured instruments to address climate change mitigation. They function on an international, national, or even subnational level. The premise of their function is an economic viewpoint that market mechanisms can deliver a reduction of emissions in an economically efficient way. In carbon markets, greenhouse gas (GHG) emissions are directly priced and used as virtual tradable units. A tonne of GHG emissions (t CO_2 or t CO_2e) is represented by a carbon credit or an emission permit. *Emission permits* are issued/auctioned to regulated entities before the compliance period (year) when they will be used (issued *ex ante*). *Carbon credits* are certified by private or public organizations for a project activity which led to a reduction of emissions compared to a counterfactual scenario (issued *ex post*). Most of the credits are issued for projects in renewable energy, agriculture, and forestry. Carbon credits can be then purchased to offset emissions elsewhere (Betz et al. 2022; World Bank 2023).

The demand is driven by countries' pledges to comply with international treaties, by industries in regulated sectors complying with emission limits, or by companies and individuals offsetting their GHG emissions to support their claims of carbon neutrality in advertising and self-presentation (Broekhoff et al. 2019; Betz et al. 2022).

In general, the pricing of GHG emissions is intended as a mechanism to capture the negative externalities unavoidably arising from transactions in a market economy, such as pollution, climate change, and associated socioeconomic and environmental harms, which in carbon markets are represented by a monetary value per unit of GHG emissions (Betz et al. 2022; World Bank 2023). These aspirations of carbon markets are debated and contested mainly on the grounds of their oversimplification of complex systems, technical unfeasibility to avoid externalities of markets in a market setting, the ethics of implicit monetization of climate change harms, and the outsourcing of obligations through trade possibly crowding out spontaneous environmental motivations (Spash 2010; Sandel 2013).

The two main types of carbon trading mechanisms are:
(1) cap-and-trade systems, or emission trading systems, designed by governments;
(2) baseline-and-credit systems with private or public governance generating carbon credits used for emission offsetting (Betz et al. 2022).
Both of these mechanisms rely on assumptions of several equivalents:
(1) the equivalence of climate impacts of emissions generated by polluters, and the emissions avoided elsewhere and at a different time or over a different span of time;
(2) the equivalence of different greenhouse gasses based on the global warming potential (GWP) index calculated for a given time horizon;
(3) the equivalence of accounting methodologies for carbon credit certification and the accounting methodologies for calculation of the emissions to be offset (Spash 2010).

3.6.1 Cap-and-trade systems

In a cap-and-trade system, the government places a total maximum limit (a cap) on GHG emissions for companies in regulated economy sectors. Most often, the sectors are emission intensive and easy to measure, such as electricity and heat generation, and manufacturing industry (ICAP 2023). The emission limit equals the number of permits which are distributed and/or auctioned for a specified period. Companies submit a corresponding number of permits to cover their emissions, and then sell or buy the surplus inside the system or in a connected market (Betz et al. 2022). Reduction of emissions is then typically claimed by countries towards their commitments under the Paris Agreement (Kreibich & Hermville 2021).

The theoretical model of this system is such that at a particular price level per carbon permit, some companies will choose to invest in low-emission technologies, sell the unused permits for profit or bank them for future use, while for others, it is more cost-effective to buy extra permits instead. This way, the total emissions stay within the limit in the most cost-effective manner. The total emission limit gets more strict over time as the government reduces the number of permits (Spash 2010; Betz et al. 2022).

In practice, the effectiveness and environmental integrity of such system depends on the type and level of sanctions, the reliability of emission monitoring, reporting and verification (MRV), stringency of the cap (avoiding status quo), how are baseline emissions negotiated, how fairly are permits distributed, and other market and regulatory features. There are also competing interests between the regulated entities and the overseeing regulators in the design of the system and in information sharing (Spash 2010; Betz et al. 2022).

There are currently 28 emission trading systems covering about 17 % of global GHG emissions. There are many variations in how the system is designed, what economy sectors and GHGs are covered, whether permits are allocated for free or auctioned, or how the revenues are redistributed. Some emission trading systems function separately, some are linked together and transfer permits between them. Some jurisdictions also allow the purchase of carbon credits from international or domestic baseline-and-credit markets as a more flexible way to comply with emission limits, and some define relative emission limits per unit of output or per GDP (ICAP 2023). The current trend is that more countries are planning to establish domestic baseline-and-credit markets to supply carbon credits into the national emission trading systems or into the system of carbon taxes or for voluntary commitments (World Bank 2023).

3.6.2 Baseline-and-credit systems

In baseline-and-credit systems, carbon credits are generated by various projects which reduce GHG emissions beyond a "business-as-usual" scenario. This is a counterfactual (baseline) scenario which defines the level of emissions which would most likely occur without the activity. The difference between the baseline and the actual emissions determines the amount of carbon credits which will be issued. Carbon credits are then purchased by countries, companies or individuals seeking to reduce their emissions on the paper. The motivation for the demand is either compliance with imposed emission limits (if offsetting is permitted), or corporate and personal pledges of carbon neutrality (Spash 2010; Ahonen et al. 2022; Betz et al. 2022).

The largest volume of carbon credits is issued by private standard organizations with international reach, Verified Carbon Standard (Verra) and Gold Standard, and an international carbon trading mechanism integrated into the Kyoto Protocol overseen by the UNFCCC, the Clean Development Mechanism (CDM) (World Bank 2023).

The majority of credits is issued for land-based projects in forestry, agriculture, and in renewable energy. Some projects also supply households in developing countries with more efficient appliances, such as clean cookstoves, lighting, biogas, and water filters (ICAP 2023; World Bank 2023).

Clean Development Mechanism (CDM) of the Kyoto Protocol

The concept of carbon offsets and the demand for their purchase emerged at large with the adoption of the Kyoto Protocol in 1997, the predecessor of the Paris Agreement (Spash 2010). The Kyoto Protocol established the mechanisms for carbon trading among countries. The participating countries were divided into developed industrialised countries with imposed GHG emission limits, and developing countries without imposed limits. This created a demand on the side of developed countries and a large potential for supply from the unregulated environment in developing countries (Lang et al. 2019; Michaelowa et al. 2019). A similar but less significant mechanism enabled trading of carbon credits among developed countries, sourced typically from projects based in Eastern Europe (Spash 2010).

Besides saving the costs of compliance with emission limits, the trading mechanisms were established with additional objective of directing finances for sustainable development into developing countries and emerging economies (Michaelowa et al. 2019). Lo and Cong (2022) estimate the investments at more than 162 billion USD between 2005 and 2021. An equivalent to 1,6 billion t CO_2e of emission permits was purchased between 2008 and 2020 by countries and companies covered in the EU Emission Trading System (ETS). Since 2020, the use of these credits is no longer allowed in the EU ETS, as the limit for their use was reached (Michaelowa et al. 2019).

Voluntary carbon markets (VCM)

Voluntary carbon markets are self-governed private systems which operate alongside but independently of the policies of international climate treaties. They develop their own methodologies and rules for the certification and verification of carbon credits. Compared to carbon markets governed by public institutions, VCM as private systems depend on marketing and discursive strategy to gain relevance and trust (Lang et al. 2019; Ahonen et al. 2022). The evolution of discursive strategies and the development of new standards in response to developments in climate policy have been reviewed by Lang et al. (2019). The major storylines have included VCM being more innovative and flexible in contrast to regulated carbon trading, or having multiple social and environmental co-benefits, and thus delivering sustainable development. New storylines include raising climate ambition in contrast to countries' insufficient commitments, and "results-based finance for sustainable development" which starts to shift the purpose of voluntary offsetting from carbon-neutrality claims to investments into sustainability certificates.

Main principles

The fundamental concept for the environmental integrity of carbon credit projects is additionality. Determination of additionality refers to the process of proving that the reduction of GHG emissions would not happen, the activity would not be undertaken, without the prospects of revenue from carbon credit sales. Carbon credits should not be generated from activities which are required by the law, or activities which are, or would be, financially profitable by themselves (WBCSD & WRI 2005; Broekhoff et al. 2019). This includes practices which receive public funding, for example under the European Common Agricultural Policy (CAP) (Paul et al. 2023).

Additionality and an appropriate baseline level of emissions cannot be determined with a 100 % accuracy because the scenarios of *what would have happened* are inherently unknowable (Broekhoff et al. 2019). The approach to their determination is subject to the policy of the project developer or the designers of methodologies for their estimation. The regulatory and market environment is dynamic, regulatory requirements change and prices change, and additionality should be regularly reevaluated (WBCSD & WRI 2005; Paul et al. 2023). The validation of project documentation and verification of achieved reduction in emissions is done by third-party auditors. Throughout the structure of the voluntary carbon market, the incentives of all market players are swayed towards the production of large volumes of credits for low costs. This includes the auditors' interest to be hired again. Therefore, additionality and baselines as rather arbitrary concepts are at a particular risk of manipulation (WBCSD & WRI 2005; Betz et al. 2022).

Carbon projects have upstream and downstream effects on ecosystems and on the socioeconomic sphere due to caused shifts in financial incentives and market prices (WBCSD & WRI 2005). How the system boundaries are drawn determines which effects will be accounted for, and which will be excluded. For the same reason as the baseline emissions are at risk of being overestimated, the actual emissions resulting from a project are at risk of being underestimated – both result in the inflation of generated credits (Broekhoff et al 2019; Betz et al. 2022). Some uncertainties stemming from the project's risk of reversal are addressed by establishing a "pool" of reserve credits serving as an insurance mechanism. An insurance mechanism should be designed to cover only natural disturbances (forest fire, drought, etc.) in order not to incentivise negligence or intentional reversal (Broekhoff et al. 2019).

"Carbon leakage" is the term used for secondary effects which negate the positive impacts of a project outside of its accounting boundaries. Typical examples occur in land-based projects in forestry and agriculture (Broekhoff et al. 2019; Paul et al. 2023). For example, projects generating credits from forest preservation on one plot of land may simply cause a shift of the production of timber to a different area if the demand for timber is unchanged. Similarly, projects generating credits from reforestation may cause further conversion of natural ecosystems into arable land elsewhere. If proper measures are not taken in the certification methodology, carbon leakage may occur beyond or within the boundaries of a single farm when only certain fields are certified for carbon credits. By incentivising redistribution of organic fertilizers to these plots, the remaining fields may be negatively impacted by decreased inputs of organic fertilizers or by necessary intensification. Similar effects may occur beyond the

boundaries of a farm if purchases of external organic fertilizers or other resources significantly reduce their availability to others (Paul et al. 2023).

Carbon leakage is also caused by the carbon footprint of the entire system involved in generating carbon credits. This includes expenditures on the project development, marketing, carbon accounting, monitoring and measurements, verification, and tracking the credits in carbon registries. Increasing volumes of transactions and increasing demand for credibility lead to the use of energy-intensive systems of accounting and verification, such as the blockchain technology (Wongpiyabovoron et al. 2022; World Bank 2023).

The selection of methods and standards always involves trade-offs between the credibility for the buyers, environmental integrity (accuracy), costs of the program development, administration, and participation in the program (WBCSD & WRI 2005). The counterweight pushing for higher environmental integrity is the pressure of environmental non-government organizations (NGOs) and the buyers' demand for higher credit legitimacy to avoid their own reputational damage by purchases of low credibility credits (Broekhoff et al. 2019; World Bank 2023).

4 Material and methods

4.1 Material

In the field experiment, we used sewage sludge biochar (SSBC) collected from a wastewater treatment plant in Trutnov, Czech Republic. This wastewater treatment plant uses a pyrolysis unit Pyreg P500 (Pyreg GmbH, Dörth, Germany) for sewage sludge management. During the process, sewage sludge is dried and then pyrolyzed at 500-650 °C. Dried sewage sludge was also collected from the same facility for material analysis.

Wood biochar (WBC) was collected from a gasification plant in Zlatá Olešnice which produces biochar from used wooden pallets using a two-stage process: pyrolysis of feedstock (500-600 °C) followed by cracking of volatiles into gases (1000 °C).

Table 3. Average carbon content (%) in materials with standard deviation (n = 2).

Material	Dosage (kg/m^2)	Total mass (kg)	C_{TOT} [a] (%)	C_{OX} [b] (%)
Sewage sludge	-	-	$35,45 \pm 0,09$	$7,50 \pm 0,32$
SSBC	5,42	32,52	$27,51 \pm 2,59$	$6,98 \pm 0,05$
WBC	1,79	10,74	$88,08 \pm 0,23$	$7,09 \pm 0,03$

[a]Total C content
[b]Oxidizable C content
[c]Water extractable organic carbon

4.2 Field experiment design

The experimental plots for the field trial were established in June 2023 at the experimental site belonging to the University of Life Sciences Prague located in Prague – Suchdol, Czech Republic. Several days prior to the trial establishment, an area of approximately 12 × 9 m of permanent grassland was sprayed by herbicide and cultivated. The experiment consisted of 36 plots with an area of 1 m^2 each. Each plot was separated by a 0,5 m safety boundary from the field edges and from adjacent plots. The design is depicted in Fig. 3.

Sewage sludge biochar (SSBC) was applied at a dose of 5,42 kg/m^2 on six plots, wood biochar (WBC) was applied at a dose of 1,79 kg/m^2 on six plots, six plots served as control without any treatment, and the additional plots were used for materials which were not included in this experiment. The plots were divided into six columns, each with the same combination of treatments with randomized distribution. The materials were incorporated into soil by a rototiller into a depth of approximately 20 cm. Half of the field was sown with *Lolium perenne* and half was kept as bare fallow throughout the season. The field received water with rainfall and was also irrigated by a sprinkler about twice a week as needed.

	1	2	3	4	5	6
	1Control	2WBC	■	4Control	5WBC	■
	■	■	■	■	■	■
	■	2SSBC	■	■	5Control	■
	■	2Control	3SSBC	■	5SSBC	6SSBC
	1WBC	■	3Control	4WBC	■	6Control
	1SSBC	■	3WBC	4SSBC	■	6WBC

Figure 3. Field experiment design. Groups 1-3 were sown with perennial grassland, groups 4-6 were kept as bare fallow.

4.3 Biomass harvests

Biomass was harvested twice during the vegetation season. The first harvest was done on 16 August 2023 (8 weeks after sowing). The second harvest was done on 18 October 2023 (9 weeks after the first harvest).

The harvested area on each plot was $0,7$ m^2 and was delineated by a metal frame with dimensions of $1,0 \times 0,7$ m. The harvest was done by a combination of electrical and normal scissors at a height of around 5 cm above the ground. The harvested biomass was transferred in labelled paper bags, put into a dryer and dried at 60 °C. The rest of the field was mowed, raked, and the biomass was removed off site.

Biomass in the dryer was periodically weighed until it reached constant mass. For the final weighing of biomass yields, dry biomass was quantitatively transferred from its respective paper bags into a new bag or an appropriately sized dish of known mass.

After each weighing, the contents were ground up in an electric mill, manually homogenized, and prepared into smaller samples for subsequent elemental analysis.

4.4 Soil sampling

Soil samples were taken by a soil probe into a depth of 20 cm. First (time zero – T0) sampling was performed at the beginning of the experiment before the application of soil amendments. One soil sample was taken from each of the plots (36 samples in total), and these samples were mixed into 6 composite samples according to the assigned treatment of the plots. Only T0 SSBC, T0 WBC and T0 control composite samples were used for this experiment. A workflow diagram of initial soil sampling and subsequent analyses is shown in Fig. 4.

Second soil sampling was performed after the second biomass harvest on 20 October 2023. In this instance, 5 samples were taken from each plot and mixed into composite samples for each plot (36 composite samples, 180 soil samples in total). Only the soil samples from the SSBC, WBC and control plots were used for this experiment (90 soil samples in total, 18 composite samples). A workflow diagram of the sampling and analyses is shown in Fig. 5.

Individual samples were mixed into composite samples upon sample collection on the field. Collected samples were air dried, homogenized with a ceramic mortar and pestle, and sieved through a 2 mm sieve. Sieved soil was further manually homogenized and prepared into smaller samples for subsequent analyses.
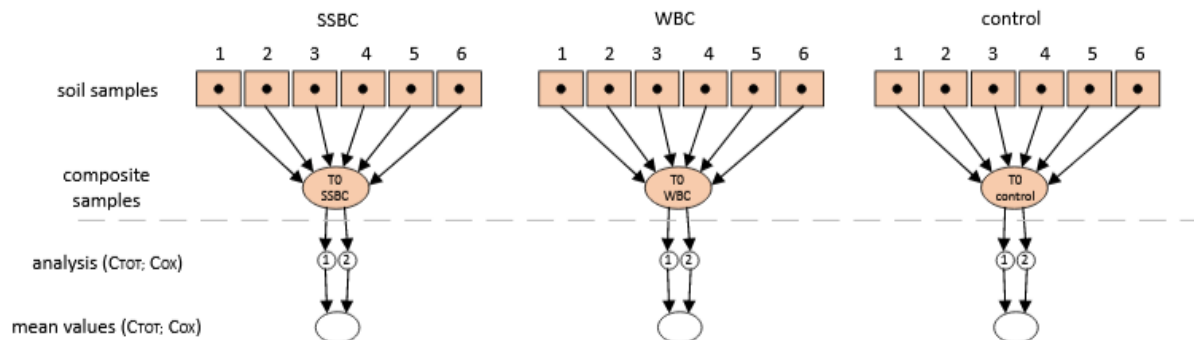

Figure 4. Sampling scheme and analysis of T0 soil samples. Grey line in diagram divides the scheme of soil sampling from analyses and calculations.
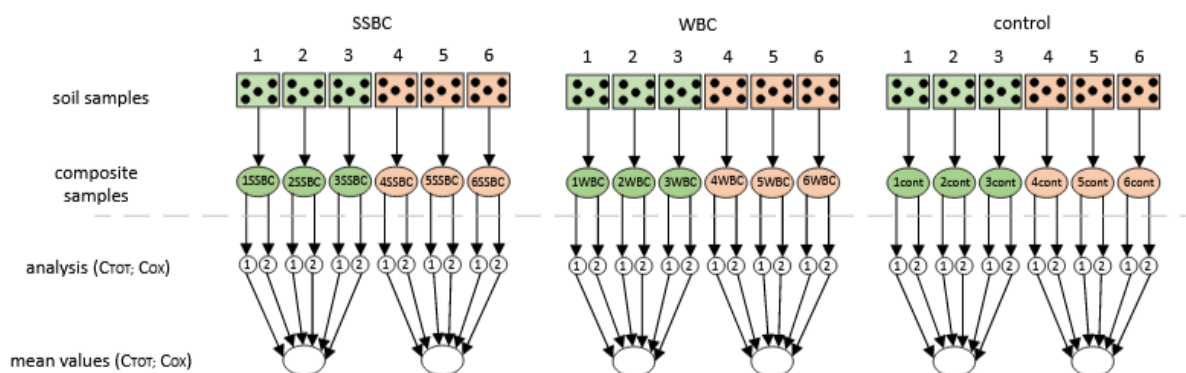

Figure 5. Soil sampling scheme and analysis of samples after the vegetation season.

4.5 Analytical methods

4.5.1 Total C content in biomass, soil, and materials

The total C content in biomass, soils, and materials was determined by dry combustion using an automatic Vario MACRO cube analyser (Elementar Analysensysteme GmbH, Hanau, Germany). Biomass and materials (sewage sludge, SSBC, WBC) were prepared for analysis as dry fine powder weighing 20-30 mg. Biomass samples were analysed in three replicates from each plot and from each harvest. Materials were analysed in two replicates. Soil samples weighed 35-40 mg and were analysed in two replicates.

4.5.2 Oxidizable C content

The content of oxidizable C (C_{OX}) in soil samples was determined by a colorimetric method based on wet oxidation of organic matter in a mixture of 2 M solution of potassium dichromate and concentrated (96 %) sulfuric acid. In the following reaction, the

orange-coloured dichromate (Cr^{6+}) is reduced to green-coloured Cr^{3+} proportionally to the amount of oxidized C:

$$2\,K_2Cr_2O_7 + 3\,C + 8\,H_2SO_4 = 2\,K_2SO_4 + 2\,Cr_2(SO_4)_3 + 3\,CO_2 + 8\,H_2O$$
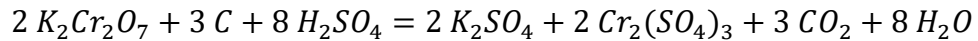
The concentration of Cr^{3+} is determined spectrophotometrically by measuring the absorbance of the solution at $\lambda = 600$ nm. This is the wavelength of maximum absorbance by Cr^{3+}, while the excess dichromate (Cr^{6+}) in the sample does not absorb light at this wavelength.

Soil samples were air dried and then dried overnight at 105 °C before weighing. The soil samples were weighed into 100 ml volumetric flasks. The mass was kept between 0,990 g and 1,017 g. A blank sample without soil was also prepared. The weight of sewage sludge and biochar samples was reduced accordingly due to their high C content.

Using a volumetric pipette, 10 ml of 2 M solution of K₂Cr₂O₇ was added, followed by 10 ml of 96 % H₂SO₄. This reaction is highly exothermic, and the procedure must be done under a fume hood. After the initial reaction, the suspension was swirled and then transferred into a sand bath heated to 135 °C. The flasks were buried in the sand and were heated for 45 minutes.

After heating, the suspension was diluted with demineralized water up to approximately 90 ml. After being left to cool to room temperature, the flasks were filled to the 100 ml mark to avoid changes in volume. The suspension was then agitated by a vortex and filtered through a filter paper into labelled beakers. A series of dilutions of sucrose (0; 5; 10; 20; 30; 40; and 50 mg C/ml) was also prepared for the construction of calibration curve.

Absorbance of the samples was measured using a Lambda 25 UV/VIS Spectrometer (PerkinElmer, Inc., Massachusetts, USA). First, demineralized water was used to zero the instrument and the sucrose dilution series was measured. The calibration curve and the formula of the regression line was generated in Microsoft Excel. Then, the absorbance of the blank sample was measured, and the value was subtracted from the values obtained for soil samples. Using the calibration curve, the results were recalculated to concentration of C (mg C/l) and then to weight-to-weight values (mg C/g of sample).

4.6   Statistical analyses and calculations

Statistical analyses of biomass yields, C content in biomass, and C_{TOT} and C_{OX} soil was done by one-way ANOVA with Tukey's HSD post-hoc test. The significance level was $\alpha = 0,05$ for all tests. When the p-values were lower than the 0,01 or 0,001 significance level, values were marked as $p < 0,01$ or $p < 0,001$. Statistical analysis was done in Microsoft Excel and IBM SPSS Statistics ver. 27.

The calculation of C balance of biochar amendments was done in relation to the initial soil C content on control plots, WBC plots, and SSBC plots. Dry bulk density of 1,3 g/cm³ of soil had to be assumed before and after the application of materials, and after the vegetation season. The C balance entails a comparison of the initial C content (C_{TOT}) in soil, C_{TOT} added in amendments (WBC, SSBC), and the sum of C_{TOT} in the system after the vegetation season (soil + biochar amendment + biomass). The results were expressed as a relative change (%) of C_{TOT} compared to the initial soil C_{TOT} (T0), and compared to the initial soil C_{TOT} + C_{TOT} in biochar (T0 + BC at T0). The same calculation was performed for the control plots without any amendment, and the same was done for all treatment versions without vegetation.

5 Results

5.1 Biomass yield and C content in biomass

The results of one-way ANOVA didn't show a statistically significant difference between the mean values obtained in I. harvest (p = 0,291), nor a significant difference between the mean values in II. harvest (p = 0,957). The sum of both harvests also didn't show a statistically significant difference between the group means (p = 0,210). Overall, the soil amendments (WBC, SSBC) didn't show a statistically significant effect on biomass yields in our field conditions. The mean values of biomass yields in I. harvest show a pattern: Control > WBC > SSBC, and an opposite pattern in II. harvest: SSBC > WBC > Control (Fig. 6.; Tab. 1. in Supplementary material).

A significant difference was found between the overreaching mean of C content (%) measured by elemental analysis for I. harvest and II. harvest (p << 0,001). The recalculation of biomass yields into their C fraction follows a similar pattern of mean values as biomass harvests alone: I. harvest (Control > WBC > SSBC), II. harvest (SSBC > WBC > Control) (Fig. 6.; Tab. 2. in Supplementary material). The difference among group means remains not significant for C_{TOT} in I. harvest (p = 0,259), C_{TOT} in II. harvest (p = 0,961), and for their sum (p = 0,178).
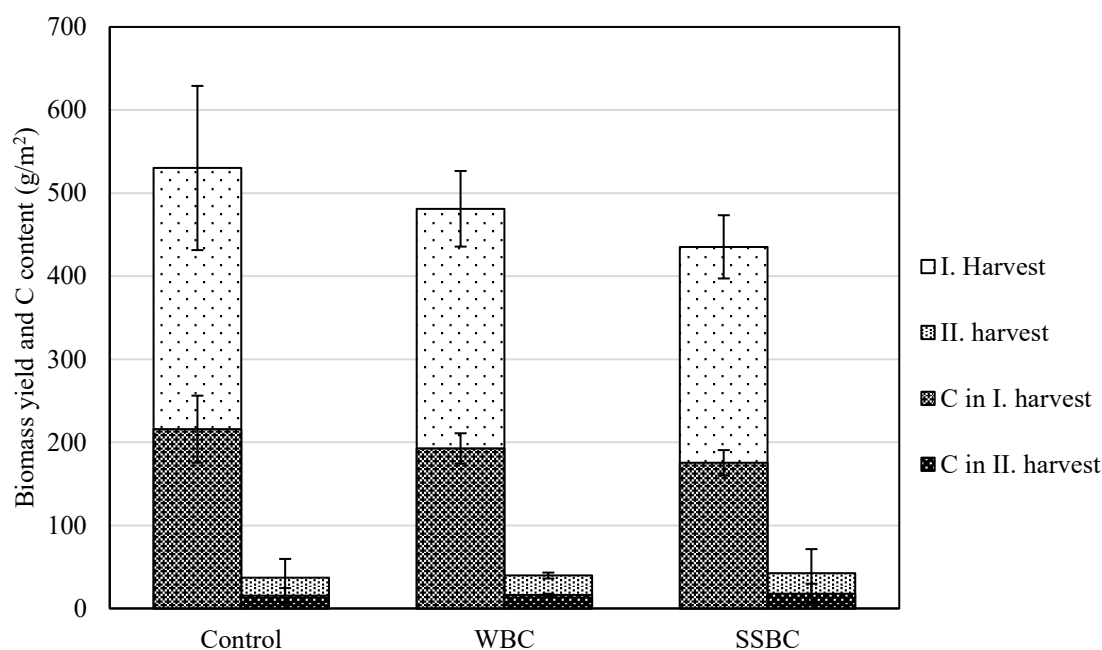

Figure 6. Average biomass yields (g/m^2) on dry matter with standard deviation (n = 3) from I. and II. harvest, and depiction of their C fraction (g/m^2). Carbon content (g/m^2) in both harvests is calculated from average biomass yields (n =3) multiplied by corresponding average value of C content in biomass (n = 9) for each group.

5.2 Soil C content

5.2.1 Initial soil C content – at T0

The initial C content in soil was determined before the application of soil amendments (before cultivation). The initial mean values of C_{TOT} in soil vary between assigned groups but these differences are not statistically significant among groups (p = 0,766). The initial mean values of C_{OX}, however, do show statistically significant differences: Control vs. SSBC (p = 0,020) and WBC vs. SSBC (p = 0,013). The C content in soil (C_{TOT}, C_{OX}) was determined in % wt., and the dosage of C added in WBC and SSBC (C_{TOT} BC, C_{OX} BC) was given per area in g/m^2. These values were recalculated to comparable units using dry bulk density of 1,3 g/cm^3 and cultivated volume of soil of 0,204 m^3.

The dosage of 1,58 ± 0,00 kg C/m^2 in WBC represents an increase of C_{TOT} by 0,59 ± 0,00 % wt. in the cultivated mass of soil (from 1,99 ± 0,12 % to 2,58 ± 0,13 %). The dosage of 1,49 ± 0,14 kg C/m^2 in SSBC represents an increase of C_{TOT} by 0,56 ± 0,05 % wt. (from 2,19 ± 0,43 % to 2,75 ± 0,43 %) (Fig. 7.). All values in g/m^2 and in % wt. are shown in Tab. 3. and Tab 4. in Supplementary material. These values are important as the baseline for further C balance calculation.

The content of C_{OX} added in WBC was equivalent to an increase of 0,05 ± 0,00 % wt. of C_{OX} in the cultivated mass of soil (from 1,14 ± 0,05 % to 1,19 ± 0,05 %), in SSBC, the increase was equivalent to 0,14 ± 0,00 % wt. of C_{OX} in soil (from 0,88 ± 0,03 % to 1,03 ± 0,03 %) (Fig. 7.). These values are also shown in Tab. 3. and Tab. 4. in Supplementary material.

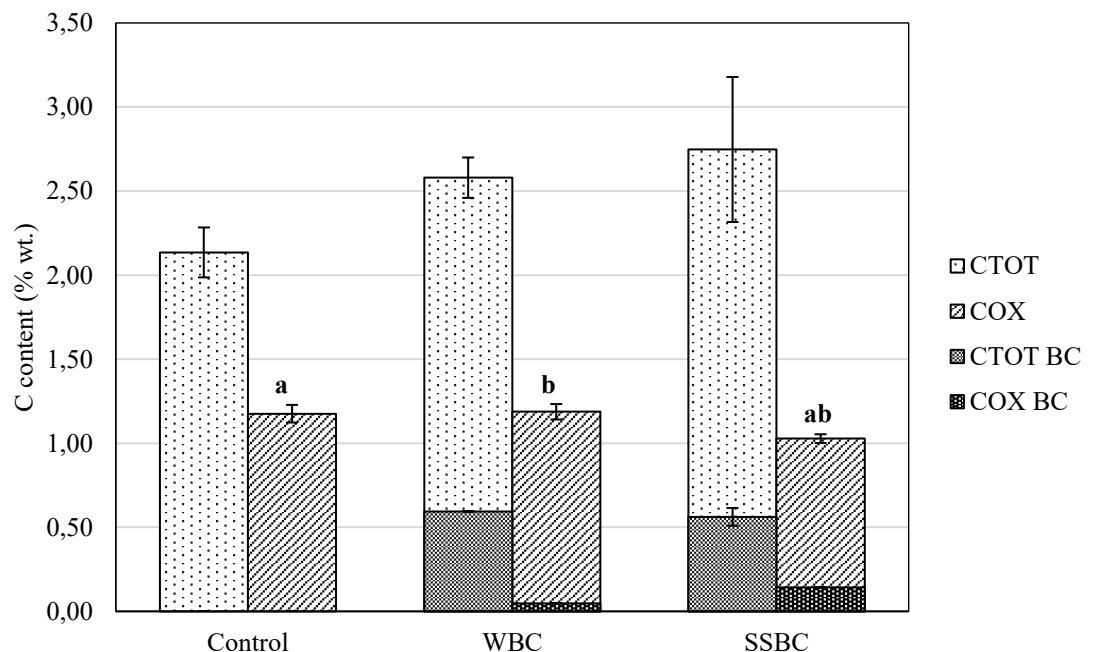Figure 7. Initial (T0) soil C content (C_{TOT}, C_{OX}) and fraction of C added in soil amendments (C_{TOT} BC, C_{OX} BC), recalculated for the cultivated volume of soil (0,204 m^3) with dry bulk density of 1,3 g/cm^3, and expressed as mean values (% wt.) with standard deviation (n = 2) (as shown in Fig. 4.). Only significant differences are visualized. The C_{TOT} BC and C_{OX} BC were not tested for significance.

5.2.2 Soil C content after the vegetation season – at T1

The C content measured in soil after the vegetation season (at T1) includes the native C content and the C added in soil amendments. Similarly as with the T0 measurements, the values were recalculated for the cultivated volume of soil (0,204 m^3) of dry bulk density of 1,3 g/cm^3 and expressed in % wt. Fig. 8. shows C_{TOT} values and Fig, 9. shows C_{OX} values.

The difference in mean C_{TOT} values on the grassland was, predictably, statistically significant ($p < 0,001$) between Control and WBC groups, and between Control and SSBC groups. The difference between WBC and SSBC groups was not statistically significant ($p = 0,785$). Similar findings applied to the C_{TOT} values on the fallow - the difference between the Control and WBC group, and between Control and SSBC was significant at ($p < 0,001$), and the difference between WBC and SSBC was not significant ($p = 0,985$). The presence/absence of vegetation was not a significant factor in either group (Control: $p = 0,321$; WBC: $p = 939$; SSBC: $p = 0,530$).
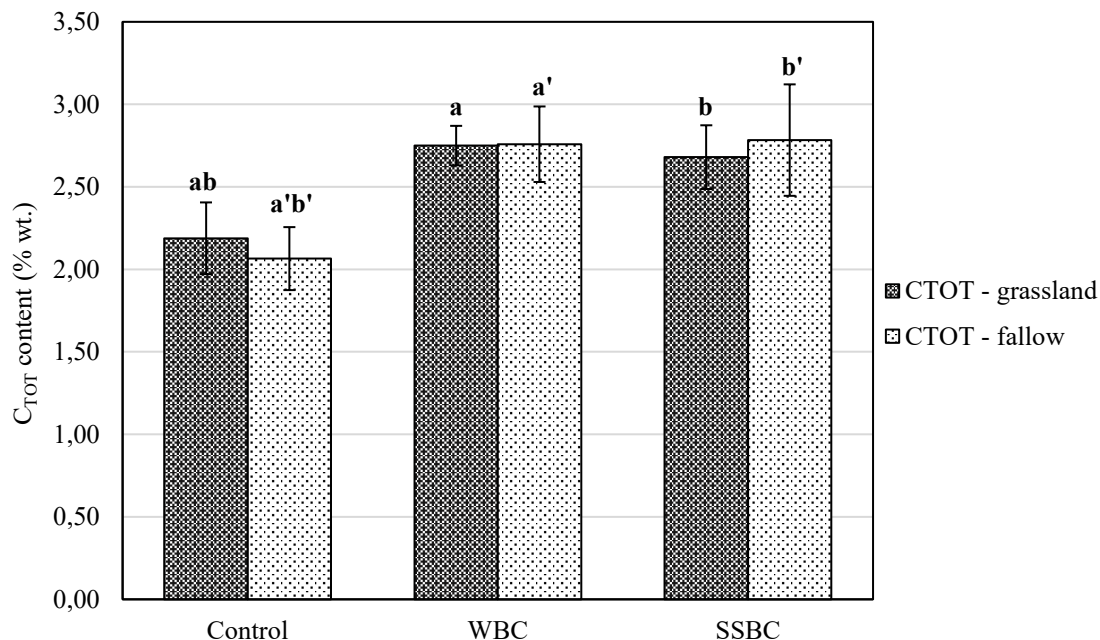

Figure 8. Total carbon content (C_{TOT}) in cultivated soil after the vegetation season (at T1). Values are expressed as overall mean (% wt.) and standard deviation (n = 6) (scheme shown in Fig. 6.). Only significant differences of two separate ANOVAs (ab and a'b') are visualized.

The content of oxidizable carbon (C_{OX}) was the highest on fallow plots amended with SSBC ($2,10 \pm 0,15$ % wt.), this value yielded a statistically significant difference in combination with any other mean C_{OX} ($p < 0,01$). The mean values of C_{OX} (% wt.) on grassland (Control: $1,21 \pm 0,35$ %; WBC: $1,49 \pm 0,19$ %; SSBC: $1,38 \pm 0,10$ %) were consistently lower than on the fallow (Control: $1,46 \pm 0,18$ %; WBC: $1,57 \pm 0,13$ %; SSBC: $2,10 \pm 0,15$ %). A significant difference was again only between the SSBC values on grassland and fallow ($p < 0,001$). Overall, the grassland plots were not significantly different ($p = 0,167$), and in the fallow plots, only the SSBC plots differed from Control ($p < 0,001$) (Control vs. WBC: $p = 0,934$). All values are shown in Tab. 5. in Supplementary material.
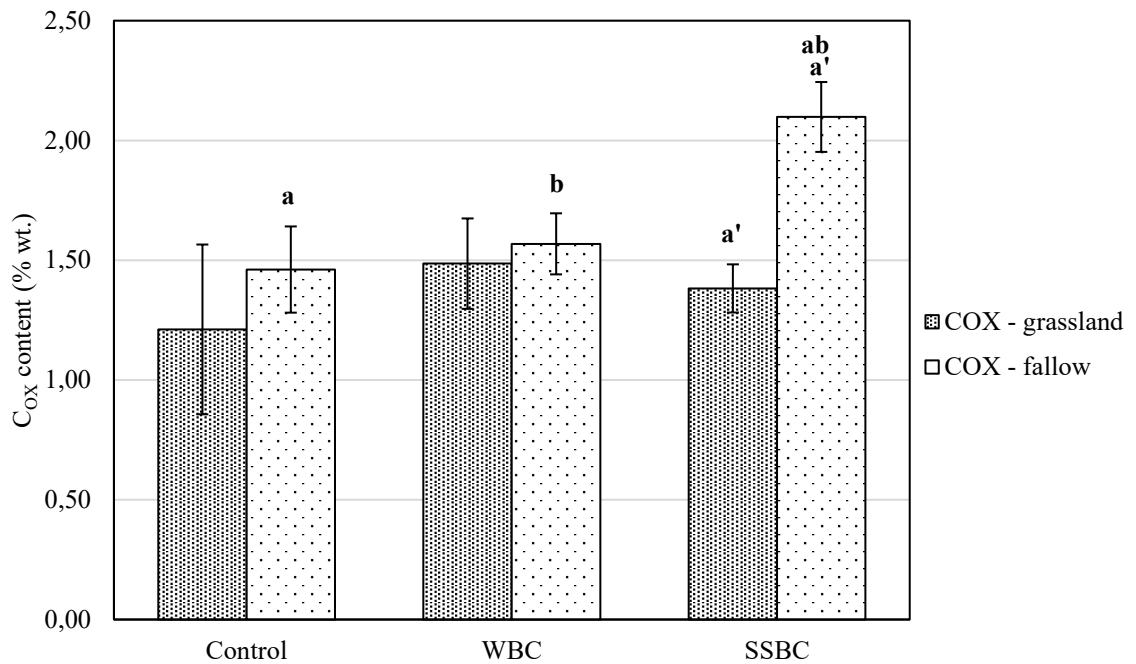
Figure 9. Content of oxidizable carbon (C_{OX}) in cultivated soil after the vegetation season (at T1). Values are expressed as overall mean (% wt.) and standard deviation (n = 6) (scheme shown in Fig. 5.). Only significant differences of two separate ANOVAs (ab and a'b') are visualized.

5.3 Carbon balance

The total amount of C added in WBC (1,58 ± 0,00 kg) represented an average increase in C_{TOT} by 29,95 % – C_{TOT} in WBC dosage was equal to about one third of the C_{TOT} in soil. The amount of C in SSBC (1,49 ± 0,14 kg) increased the C_{TOT} in soil by 25,73 % on average – C_{TOT} in SSBC dosage was equal to about one third of the C_{TOT} in soil. These values are shown in Fig. 10. as "BC at T0". Control plots received no amendment, so this entry is left blank.

Fig. 10. also shows relative change in C_{TOT} measured after the vegetation season (end – grassland, end – fallow), this time without a distinction of C_{TOT} in amendments and soil. The plots on grassland also included the additional C in both harvests (biomass C). The values are always expressed in %, relative to the initial state for the particular group (changes on Control plots are compared with T0 soil on Control plots, changes on WBC plots are compared with T0 soil on WBC plots, etc.).

While the control plots on the fallow on average lost some C (- 3,28 %) and gained C on the grassland (+ 2,50 %), this pattern didn't repeat for plots with WBC or SSBC. Relative to the initial sum of C_{TOT} (T0 soil + BC at T0), C_{TOT} increased (+ 6,61 %) on the WBC grassland and decreased (- 2,45 %) on the SSBC grassland. Contrary to expectation, the values were higher on the fallow plots for WBC (+ 6,93 %) and SSBC plots (+ 1,31 %) (Fig. 11.).

The sum of biomass C increased the relative gain on the Control plots (+4,08 %), increased the gain on the WBC plots (+ 3,97 %) over the WBC fallow (Fig. 10.), and compensated the relative loss (- 2,45 %) measured on the SSBC grassland by + 2,65 % increase (Fig. 11.).
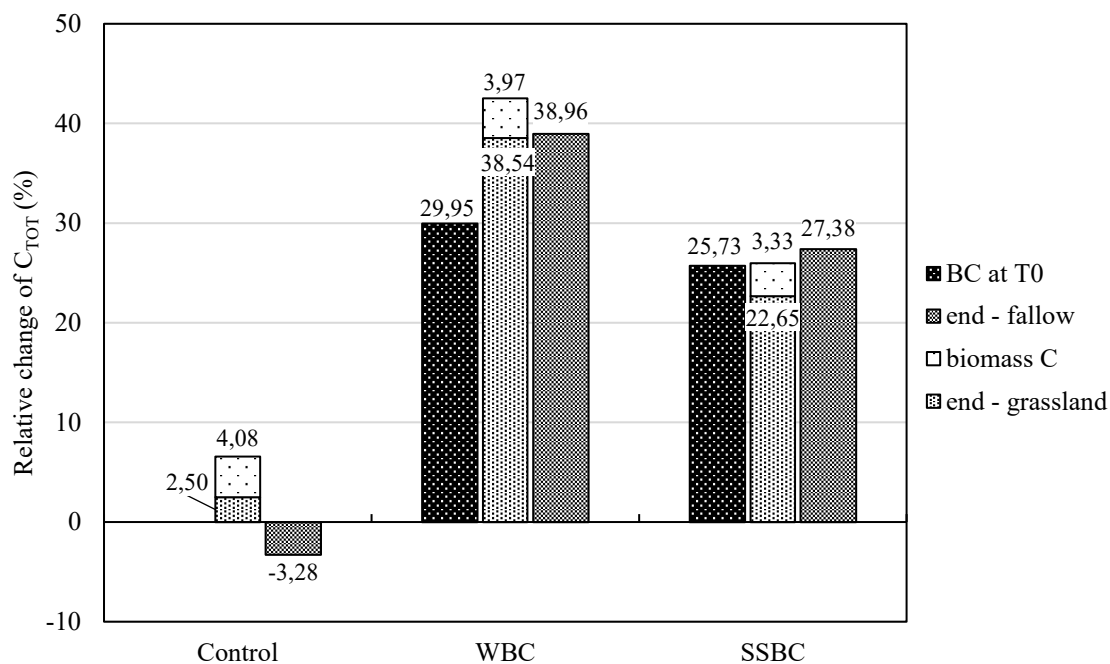
Figure 10. Relative change (%) in C_{TOT} compared to respective initial T0 C_{TOT} values measured before the application of soil amendments.
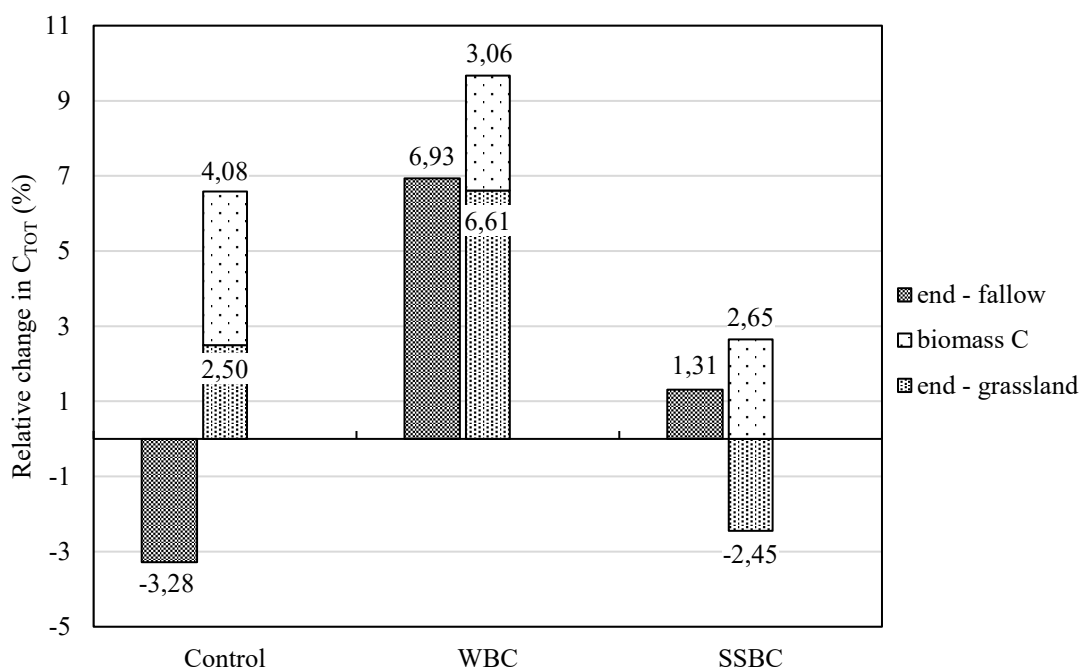

Figure 11. Relative change (%) of C_{TOT} compared to respective initial T0 + BC values of C_{TOT} in soil.

6 Discussion

This field experiment studied the effect of biochar amendments on the biomass yields of *Lolium perenne* in two separate harvests during the vegetation season. Because the aim of the experiment was to calculate the overall C balance, the total C content in biomass was measured by dry combustion and expressed as total C (C_{TOT}) in g/m^2 and % wt. Similarly, the values of C content in soil and in soil amendments (WBC, SSBC) were expressed in g/m^2 and % wt. for consistency, and only the C_{TOT} values obtained by dry combustion method were used in the overall C balance.

The boundaries of this experiment were too narrow and non-pyrolyzed sewage sludge was not used as organic amendment to allow a direct comparison in the C balance. Alternative methods of sewage sludge treatment and a comparison with pyrolysis are therefore discussed more universally using recent literature.

6.1 Biomass yield and C content in biomass

In our field experiment, we measured the dry-matter yield of above-ground biomass in two separate harvests and calculated the total C content in biomass in g/m^2. The results of our experiment didn't show a significant influence of biochar amendments (5,42 kg/m^2 SSBC; 1,79 kg/m^2 WBC) on the dry-matter yields of the above-ground biomass. This was true for the total biomass yields, and for the yields of separate harvests. However, these results are based on a small number of replicates for each treatment in each harvest (n = 3) and there were large variations in biomass yields between plots, and a disproportionate mass distribution between I. harvest and II. harvest. We hypothesized that biochar soil amendments would lead to differences in biomass yields, either in the sense of an increase, or a decrease compared to control. Both contrasting effects have been reported in literature and have been attributed to numerous factors - combinations of biochar and soil properties, plant species, and environmental conditions (Jeffery et al. 2011). Increased growth of *L. perenne* was reported by Schimmelpfennig et al. (2014) in a greenhouse pot experiment using soil amended with non-carbonized feedstock (*Miscanthus×giganteus*), hydrochar, biochar, and mixed hydrochar-biochar substrate (all equivalent to 16 ± 4 % increase of SOC). Significant increase in yields in soils amended with biochar (n = 4) and hydrochar (n = 4) was attributable to increased water-holding capacity and decreased gaseous losses of nitrogen. Increased water-holding capacity in soils is a mechanism which may improve crop productivity in sandy soils (Basso et al. 2013) and may lead to improved productivity under reduced irrigation regimes, and therefore may be beneficial through water savings (Akhtar et al. 2014). According to Saarnio et al. (2013), biochar amendment stimulates plant growth (*Phleum pratense*) during dry periods by increased soil moisture, increased C mineralization, and N uptake by plants. Plants compete with soil microbes for N which corresponds to decreased N_2O efflux. In bare soil, the biochar amendment increased soil moisture, and therefore also increased the soil respiration and N_2O efflux.

Improved mineral nutrition after sewage sludge biochar amendment was reported by Yue et al. (2017) as a mechanism leading to increasing biomass yields of turf grass grown in urban soil. The increase was proportional to increasing dosage of sewage sludge biochar (0 %, 1 %,

5 %, 10 %, 20 %, and 50 %, in mass ratio). Biochar produced from animal manure or sewage sludge (biosolids) typically contains the greatest available nutrient concentrations compared to biochar from other feedstocks (wood, crop residues, grasses) (Joseph et al. 2021). In our experiment, we expected that higher nutrient content in sewage sludge biochar (SSBC) than in wood biochar (WBC) would promote an increase in yields on the plots with SSBC. The results of our experiment, however, didn't indicate a significant difference between the two biochar amendments. Although not statistically significant, the mean values of the sum of biomass harvests (I. + II.) decreased in the pattern of: Control > WBC > SSBC, the same applied to I. harvest in separate analysis, and II. harvest had a directly opposite pattern.

Possible negative effect of biochar amendments on biomass yields has been associated with decreased N uptake due to N immobilization (Asai et al. 2009), Al toxicity or a decrease of some micronutrients (Cu, Fe, Mn) (Laghari et al..2015), phytotoxic compounds initially suppressing germination (Borchard et al. 2014), or by a disbalance between water and gaseous phases caused by excessive biochar application into fine textured soil (Castellini et al. 2015). All these effects are dependent on many variables stemming from the countless combinations of soil types, environmental conditions, land management practices, crop varieties, feedstocks used for biochar production, and the pyrolysis parameters (Jeffery et al. 2011). This warrants attention when choosing biochar as soil amendment in particular conditions. What might be seen as improvement in soil parameters (e.g. water-holding capacity) may not translate into improved crop productivity (Borchard et al. 2014).

6.2 Soil C content

In this experiment, the initial soil C content (C_{TOT}, C_{OX}) in soil was measured in % wt. and recalculated for soil volume of 0,204 m^3 (1,2 × 0,85 × 0,2 m) and dry soil bulk density of 1,3 g/cm^3. These were measured separately for the control plots, WBC plots, and the SSBC plots. These initial values varied but the differences were assessed as not significant. The dosage of WBC and SSBC was approximated to contain a comparable amount of C_{TOT} per unit of area (g/m^2). However, our C_{TOT} measurements in SSBC and WBC varied and produced different initial values of C_{TOT} applied into soil. The values of C_{TOT} on the control plots showed a decrease on the fallow (- 3,28 % relative to T0 soil), possibly due to soil cultivation which followed after the initial soil sampling. This effect can be expected to have occurred on the whole field, however, the interaction between biochar amendments and tillage-induced emissions would require a separate study. The control C_{TOT} values on grassland showed a slight increment (+ 2,50 %) compared to the T0 C_{TOT}, however, without statistical significance. The decrease of C_{TOT} observed on the fallow, and the increase on the grassland was also not statistically significant but the pattern (C_{TOT} fallow < C_{TOT} T0 < C_{TOT} grassland) followed logical expectation.

The C_{TOT} values on the WBC plots showed a relative increase of C_{TOT} after the vegetation season, both on grassland (+ 38,54 %) and on the fallow (+ 38,96 %). In both instances, these values were higher than the initial increase of C_{TOT} from WBC amendment alone (+ 29,95 %). While on the WBC plots with vegetation, this increase could be explained by root deposits incorporated into the soil samples, similar increase of C_{TOT} on the bare fallow indicates a possible methodological mistake or an unknown variable in the field conditions. This pattern

was not found on the SSBC plots, which, in comparison with C_{TOT} added in SSBC amendment (+ 25,73 %) showed a relatively lower C_{TOT} on grassland (+ 22,65 %) and a relative increase of C_{TOT} on the fallow (+ 27,38 %). Besides possible variations in field conditions, there are several possible effects on the soil C content after biochar application into soil which may be a source of variation. Studies of isotopically labelled biochar suggest that portions of biochar with lesser degree of condensation undergo initially intensive biological decomposition with decreasing rate over time. Decomposition rate also decreases with higher C content, higher pyrolysis temperature or with higher clay content in the soil (Wang et al. 2015). The materials used in this experiment were produced at a comparable pyrolysis temperature range (500–650 °C) but varied in their C_{TOT} (88,08 ± 0,23 % wt. for WBC, 27,51 ± 2,59 % wt. for SSBC), this could lead to slower rate of degradation of WBC. Other factors influencing biochar persistence include temperature and moisture regime, soil type, texture, pH and mineralogy, tillage, additional organic matter inputs, and vegetation fires (Lehmann et al. 2009). The presence of vegetation may also influence the interactions between biochar and microorganisms in soil. The stimulation of microbial activity by continuous addition of root exudates may lead to co-metabolism of biochar in the rhizosphere (Kuzyakov et al. 2015). Similarly as the presence of labile substrates may lead to co-metabolic decomposition of biochar, the addition of biochar itself has an effect on the native soil carbon content (priming effect) resulting in increased or decreased SOC mineralization which is also mediated by microbial communities (Wang et al. 2015; Rasul et al. 2022). The occurrence and the extent of all these interactions would require a separate study.

As previously described, biochar does undergo biotic and abiotic degradation in soil, but its increased resistance to biological and chemical degradation poses a challenge in soil and material analysis. This experiment included measurements of C_{OX} determined by wet oxidation using a potassium dichromate and sulfuric acid mixture with subsequent heating, which is a method routinely used in soil analysis for the estimation SOC. In soils with a significant amount of charred matter however, this method leads to underestimation of SOC due to the relative resistance of black carbon to dichromate oxidation (Hardy & Dufey 2017). The Walkley-Black method (dichromate oxidation without heating and with a 1,32 correction factor) has been proposed as a method for the estimation of SOC and black carbon by Kurth et al. (2006) who reported 20 % oxidation of fresh charcoal and suggested calculating SOC by difference. Hardy and Dufey (2017) estimated a 23,6 % oxidation of fresh charcoal, which increased to around 65 % for aged charcoal, and to around 90 % for both with subsequent heating - Anne's method (Anne 1945), and they concluded that these methods discriminate poorly between SOC and black carbon. The fraction of black carbon that is oxidized, therefore, depends on the material alteration in the environment (Ascough et al. 2011; Hardy & Dufey 2017), the conditions during the analytical procedure (Hardy & Dufey 2017), the pyrolysis temperature (Ascough et al. 2011), and on the original feedstock and particle size (Skjemstad & Taylor 2008). As is evident from the C_{OX} measurements of our materials (WBC, SSBC) and increases of C_{OX} measured in the soil samples, charred materials do undergo chemical oxidation. Besides the expected losses of WBC and SSBC due to partial mineralization in soil, it can be expected that the remaining portion of amendments in soil responded differently to dichromate oxidation than the fresh materials prepared for analysis, and the particle size distribution varied also.

6.3 Carbon balance and alternative uses

The fuel characteristics and other parameters of sewage sludge and SSBC have been previously published by Fuka et al. (2021) who also calculated the mass and energy balance of the drying and sludge pyrolysis at our selected facility. Their values of C content measured on dry basis in sewage sludge (32,3 %) and SSBC (24,5 %) vary by approximately 3 % from the average values of our respective C_{TOT} measurements of $35,45 \pm 0,09$ % and $27,51 \pm 2,59$ %. Following with a calculation of C balance using 57,16 % mass conversion from dry matter of sewage sludge input ($\approx 2,38$ t/day) to SSBC output ($\approx 1,36$ t/day), as given by Fuka et al. (2021), the pyrolysis process results in the loss of $\approx 0,44$ t C/day into the atmosphere. Using the conversion factor of 44/12 from C to CO_2, this represents emissions of $\approx 1,6$ t CO_2/day ($\approx 0,47$ t C/day, or $\approx 1,72$ t CO_2/day according to our measurements). The primary aim of the pyrolysis unit used in this facility is the production of biochar with C content equivalent to 0,33 t C/day, or $\approx 1,22$ t CO_2/day which would remain non-emitted ($\approx 0,37$ t C/day, or 1,37 t CO_2/day by our measurements). The ratio of C emitted to C stored is roughly 1,3:1.

Counting only the plots where biochar was used as soil amendment for vegetation growth, the amount of SSBC was 16,26 kg which corresponds to $\approx 3,98$ kg C ($\approx 14,59$ kg CO_2) or to $\approx 4,47$ kg C ($\approx 16,40$ kg CO_2) according to our measurements, which would be counted as emission avoidance on the outset. This amount of biochar is produced by pyrolysis from 28,455 kg of dry sewage sludge, during which $\approx 19,01$ kg CO_2 (or $\approx 20,59$ kgCO_2) is emitted. While the emissions of CO_2 arising from sewage sludge decomposition/incineration are considered to be of biogenic origin, and therefore their climate impact is not counted in most Life Cycle Assessment (LCA) studies, LCA studies focusing on resource recovery (N, P, C or energy) also apply substitution of conventional resources and fossil fuels to account for the benefits of resource recovery, and include the drawbacks of each strategy (Heimersson et al. 2016). Lundin et al. (2004) include biogas utilization for internal use at the facility and the agricultural use of sludge then substitutes N and P fertilizers. Cao and Pawlowski (2013) used biogas and pyrolysis oil to offset electricity and heat from natural gas and oil, or vehicle fuel, and compared land and landfill application of biochar. The land application included benefits of fertilizer substitution and reduction of N_2O emissions. Our field experiment didn't show any significant improvement in biomass yields which could justify including fertilizer substitution as a benefit of either biochar, even though SSBC contains a substantial amount of P and other nutrients (Fuka et al. 2021). This would require a more detailed study of the availability of nutrients retained in the material and of the predictability of their release over longer timeframe.

The lower heating value (LHV) of the dry sewage sludge used in our experiment is 13,3 MJ/kg. With the throughput of dry sludge of 743,75 t/year, this corresponds to $\approx 9891,88$ GJ/year. This amount of energy exceeds the energy requirements for the sewage sludge drying (21,09 GJ/day or 7697,85 GJ/year), which is a necessary step for incineration and pyrolysis alike. Incineration of sewage sludge with energy recovery could potentially cover the energy requirements for sludge drying and become a supplier of the surplus energy ($\approx 2194,03$ GJ/year). When our facility focuses on biochar production, this energy is used to power the pyrolysis unit and supply 43,77 % of heat into the sludge dryer with no other use for energy recovery, and the rest of the energy required for drying ($\approx 4328,9$ GJ/year) must be supplied from the district heating system, which uses energy from the coal-fired power- and

heating plant Poříčí with minor biomass co-firing (Skupina ČEZ n.d.). In sum, the energy from sewage sludge incineration could replace 6522,93 GJ/year of energy from other sources compared to pyrolysis for biochar production (avoided use of energy from the district heating system + generated surplus). Using the 2023 Czech national emission factors (EF) (tCO_2/TJ, including oxidation factors) (MŽP 2023) and assuming that sewage sludge is a renewable and carbon-neutral source of energy, the emissions avoided would be $\approx$ 638,72 tCO_2/year (if brown coal/lignite is replaced), $\approx$ 596,20 tCO_2/year (if black coal is replaced), and $\approx$ 361,70 tCO_2/year (if natural gas is replaced). Using only the values given by Fuka et al. (2021), the annual production of 425,3 t of biochar with 24,5 % C content leads to emission avoidance of 382,06 tCO_2/year before soil application. By the virtue of this, biochar production in this facility is a net climate change contributor compared to sewage sludge incineration used for fossil fuel substitution. That is unless the fuel replaced by the energy surplus is natural gas and if the district heating system also used natural gas (or any fuel mix with EF lower than $\approx$ 58,57 tCO_2/TJ, which is only slightly over the EF = 55,45 tCO_2/TJ for natural gas) (MŽP 2023). Using low-emission fuels or renewable energy to power this process would also carry an opportunity loss to serve as a substitution of higher-emitting fuels instead. The result of this comparison could be expected when the design of the process doesn't produce any energy output from the energy input (here dry sewage sludge) and the whole process of biochar production requires additional supply of energy.

In any case, the C content in biochar remains non-emitted, as is true for any fuel as long as it remains not oxidized. However, the LHV of 8,9 MJ/kg in SSBC (Fuka et al. 2021) also represents an energy loss and an opportunity loss to replace other fuels. The energy embedded in biochar is 3785,17 GJ/year. Producing the same amount of energy from lignite/brown coal emits $\approx$ 370,64 tCO_2, $\approx$345,96 tCO_2 from black coal, or $\approx$ 209,89 from natural gas. If biochar were considered a carbon-neutral biofuel like charcoal, this substitution would represent a climate benefit. When biochar is produced for carbon sequestration (382,06 tCO_2/year) and it remains unused as biofuel, this number should be accordingly reduced to account for the opportunity loss. If biochar C mineralization in soil should exceed $\approx$ 2,99 %, $\approx$ 9,45 %, or $\approx$ 45,06 % in a relevant timeframe, this would negate any emission reduction in the respective scenarios which include the opportunity loss.

If biogenic emissions from sewage sludge were included in the scenarios of incineration and pyrolysis, the EF of dry sewage sludge would be $\approx$ 89,05 tCO_2/TJ, which is slightly lower than EF = 91,04 tCO_2/TJ for black coal (MŽP 2023). Including biogenic emissions in the calculations could open up possibilities to optimize the fuel mix used for drying or for powering the pyrolysis unit (choosing fuels with lower EF) and using dry sewage sludge or pyrolysis oil and gas as replacements of fuels with higher EF. Regarding the energy losses which unavoidably arise in biochar production, Gaunt and Lehmann (2008) compared bioenergy production from dedicated energy crops and a process optimized for biochar production, and calculated the electricity losses close to 2800 MWh annually in a facility with a throughput of 16 000 t of dry feedstock producing 4 800 t of biochar. They concluded that the financial viability of such enterprise rests on the potential revenue from carbon markets and on the status of the market for biofuels.

7 Conclusions

- The proclaimed climate benefits of biochar production rest on a particular approach in carbon accounting and life-cycle assessment used in methodologies for the certification of carbon credits, not on physical science. Negative emissions of biochar production are achieved by a combination of two assumptions: the inherent carbon neutrality of biomass combustion, and the avoidance of future emissions from biomass decomposition or combustion.

- Pyrolysis of biomass for biochar production is an energy-intensive process which converts organic matter into a biologically more resistant form with an aim of its permanent disposal from ecosystems to prevent reemission of CO_2 into the atmosphere. This contradicts the principles of circular economy which prioritizes prevention, reuse, material recovery, and energy recovery from waste in this order, and direct disposal is discouraged. Biochar production incentivised by policy or revenues from carbon credits may outcompete a more rational use of local resources, cause environmental damages, and exacerbate climate change by immediate release of CO_2 during combustion. Proposed strategies for biochar production which include saving biomass from decay in ecosystems, growing dedicated crops and trees on agricultural land, and denying the return of residues and other organic matter into agricultural and forest soil may increase the vulnerability of ecosystems and human livelihoods to climate change, and decrease the resilience of natural carbon sinks.

- Without proper precaution in certification methodologies, revenues form carbon credits for soil carbon sequestration may incentivise inefficient redistribution of organic fertilizers and other natural resources into soil. Methodologies for the certification of biochar carbon credits use a decay model and require knowledge of the biochar properties, and land application serves as insurance against energy use. Per the IPCC recommendations, the stock-change method used for soil carbon sequestration by organic fertilizers and improved land management is not applicable to biochar due to its persistence.

- The field experiment didn't show a significant effect of biochar amendments (SSBC, WBC) on biomass yields of *Lolium perenne*, nor a significant difference between the effects of the two amendments which could justify the inclusion of fertilizer substitution as a benefit in a life-cycle assessment.

- Biochar amendments increased the total carbon content (C_{TOT}) and its oxidizable fraction (C_{OX}) in soil. This fact and the material analysis both show that biochar is partially oxidized by dichromate-acid mix during soil analysis. Determination of biochar persistence and its effect on the native soil matter, and the interactions with vegetation and soil biota would require using methods which would allow their quantification and qualitative distinction.

- Claiming a climate benefit requires an assessment of environmental impacts of resource extraction, weighing the benefits and impacts of alternative uses of the resource with a careful assessment of the life-cycle emissions of the technology processes, and weighing the impacts and benefits if the intended use within the same framework. By this approach, biochar production from sewage sludge in our selected facility is a climate change contributor compared to incineration with energy recovery, depending on the fuel mix used for sludge drying, and on the fuel replaced by the surplus energy from incineration.

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