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Habilitační práce

Půdní organická hmota a její vliv na úrodnost půd

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Předmluva a poděkování

Na tomto místě bych rád poděkoval svým spolupracovníkům, rodině a přítelkyni, bez nichž by tato práce nevznikla. Zvláštní dík patří prof. Ing. Ladislavu Kolářovi, DrSc. za všechny rady, zkušenosti a znalosti, jež mi předal.

Následující text bych uvedl dvěma nadčasovými citáty, které s tématem organické hmoty a půdní úrodnosti nepochybně souvisejí a výstižně naznačují charakter myšlenek, jež jsou v práci obsaženy.

„It is the decay of organic matter, and not the mere presence of it, that gives "life" to the soil“ (Hopkins, 1910).

„Attempting to hoard as much organic matter as possible in the soil, like a miser hoarding gold, is not the correct answer. Organic matter functions mainly as it is decayed and destroyed. Its value lies in its dynamic nature“ (Albrecht, 1938).

Obsah

1 Úvod

Půda je nezastupitelným výrobním faktorem v zemědělské produkci napříč kontinenty. Tato dynamicky se vyvíjející část zemského povrchu obsahující jak minerální, tak i organický materiál, je ovlivněna nespočtem fyzikálních, chemických a biologických činitelů. Odehrává se v ní řada složitých procesů včetně přeměn organických látek. Právě obsah půdní organické hmoty a její kvalita jsou jedním z faktorů, které ovlivňují úrodnost půdy. Tedy její schopnost zabezpečovat nezbytnými podmínkami existenci a reprodukci zemědělských plodin.

Organická hmota působí na fyzikální i chemické vlastnosti půdy, ovlivňuje i složení půdní bioty. Jsou-li půdy dobře zásobeny organickou hmotou, mají vyšší schopnost vyrovnávat výkyvy počasí. Půdní organická hmota má význam nejen na úrovni lokální (půdní úrodnost, zachování ekologických funkcí půdy), ale také globální (obsah uhlíku v atmosféře). Snižování obsahu půdní organické hmoty je proto jedním z hlavních faktorů vedoucích k degradaci ekosystémových služeb a snížení odolnosti terestrických ekosystémů.

Od dob, kdy se vědci půdní organickou hmotou začali zabývat, tedy zhruba od počátku 19. století, došlo v této oblasti výzkumu ke značnému pokroku. Zpočátku se v půdních vzorcích stanovoval pouze celkový ogranický uhlík v laboratoři (nejdříve na „mokré cestě“, později i „suchou cestou“), dnes je možné měřit půdní vzorky přímo v terénu například spektroskopickými metodami NIRS (400–2500 nm) a MIR (2500–25000 nm), laserem indukovanou spektroskopií LIBS, metodou INS (nepružný rozptyl neutronů), či dálkovým průzkumem Země. Pro kvalitativní analýzy půdní organické hmoty se v současnosti využívají moderní technologie, mezi něž patří například vysokoúčinná vylučovací chromatografie (HPSEC), plynová chromatografie-hmotnostní spektrometrie (GC-MS), pyrolýzní plynová chromatografie-hmotnostní spektrometrie (pyr-GC/MS), nukleární magnetická rezonance (NMR), iontová cyklotronová rezonanční hmotnostní spektrometrie s Fourierovou transformací (FTICR-MS) nebo elektrosprejová ionizační iontová cyklotronová rezonanční hmotnostní spektrometrie s Fourierovou transformací (ESI-FTICRMS). Přesto zůstává množství mechanismů transformace půdní organické hmoty neobjasněno.

V průběhu let se objevilo nepřeberné množství vědeckých prací, které popisovaly půdní organickou hmotu a její složky odlišně. V důsledku toho vznikla i nejednotná terminologie, což v praxi může vést k řadě nedorozumění. Někdy může být obsah organického uhlíku považován za celkové množství organické hmoty, jindy za množství humusu a tak podobně. Je tedy třeba věnovat pozornost tomu, jak daný autor půdní organickou hmotu dělí, jaké látky považuje za humus a tak dále.

Ačkoli je význam laboratorních analýz pro pochopení významu a přeměn půdní organické hmoty nezpochybnitelný, v praktickém zemědělství nejsou výstupy některých prací fakticky využitelné. Zemědělská praxe vyžaduje jednoduchá doporučení, která povedou k udržení či zvýšení půdní úrodnosti jak v krátkodobém, tak i dlouhodobém horizontu.

Johnston et al. (2009) si položili tyto otázky: Je půdní organická hmota důležitá pro úrodnost půdy? V jakém časovém horizontu a s jakými zemědělskými postupy se obsah půdní organické hmoty mění? Lze identifikovat, oddělit a kvantifikovat různé půdní faktory, které k „efektu organické hmoty“ mohou napomoci?

Tato práce hledá na podobné otázky odpovědi. Dává si za cíl přispět k prohloubení znalostí o vlivu půdní organické hmoty na vlastnosti půdy a její úrodnost. Představuje též řadu poznatků z oblasti výroby a využití biocharu. V neposlední řadě je v práci srozumitelně vysvětleno názvosloví používané v souvislosti s výzkumem půdní organické hmoty, které je v důsledku desítky let trvajícího bádání velmi nejednotné, někdy až zavádějící.

Introduction

Soil is a non-renewable factor in agricultural production across continents. It is a dynamically evolving part of the earth's surface, containing mineral and organic material influenced by countless physical, chemical and biological factors. Many complex processes take place in it, including transformations of organic substances. It is the content of soil organic matter and its quality that affect soil fertility, i.e. its ability to provide the necessary conditions for the existence and reproduction of agricultural crops.

Organic matter affects the physical and chemical properties of the soil and the consisting of the soil biota. If soils are well supplied with organic matter, they have a higher ability to balance weather fluctuations. Soil organic matter is essential not only at the local scope (soil fertility, preservation of the ecological functions of the soil) but also at the global scope (carbon content in the atmosphere). Decreasing soil organic matter content is one of the main factors leading to the degradation of ecosystem services and the reduction of the resilience of terrestrial ecosystems.

Since scientists began dealing with soil organic matter (roughly from the beginning of the 19th century), considerable progress has been made in this area of research. Initially, only the total organic carbon was determined in the laboratory (first in the "wet oxidation", later also in the "dry combustion"). Today it is possible to measure soil samples directly in the field, for example, using spectroscopic methods NIRS (400–2500 nm) and MIR (2500–25000 nm), laser-induced breakdown spectroscopy (LIBS), the INS method (inelastic neutron scattering), or remote sensing. Nowadays, modern technologies are used for qualitative analyses of soil organic matter. It includes, for example, high-performance size exclusion chromatography (HPSEC), gas chromatography-mass spectrometry (GC-MS), pyrolysis gas chromatography-mass spectrometry (pyr-GC/MS), nuclear magnetic resonance (NMR), Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) or electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI-FTICRMS). Nevertheless, the number of mechanisms of transformation of soil organic matter remains unexplained.

Over the years, many scientific works have described soil organic matter and its components differently. As a result, different terminology also arose, which can lead to misunderstandings in practice. Sometimes the content of organic carbon can be considered the total amount of organic matter. Other times the amount of humus, and so on. It is, therefore, necessary to pay attention to how the given author divides soil organic matter, what substances he considers to be humus, and so on.

Although the importance of laboratory analyses for understanding the meaning and transformations of soil organic matter is indisputable, the results of some works are not usable in practical agriculture. Agricultural practice requires simple recommendations that will lead to maintaining or increasing soil fertility in both the short and long term.

Johnston et al. (2009) asked the following questions: Is SOM important in soil fertility? Over what time scales and with what farming practices do SOM contents change? Can the various soil factors that might/can contribute to the "organic matter effect" be identified, separated, and quantified?

This work is looking for answers to similar questions. It aims to contribute to the deepening of knowledge about the influence of soil organic matter on soil properties and fertility. It also presents many findings from the production and use of biochar. Last but not least, the work clearly explains the terminology used in connection with soil organic matter, which, as a result of decades of research, is very inconsistent, and sometimes even misleading.

2 Půda, půdní organická hmota a její význam

2.1 Půda a půdní organický uhlík

Půda, nezastupitelná složka životního prostředí. Nenahraditelný výrobní faktor v zemědělské produkci, ale také poskytovatel řady významných ekosystémových služeb. Tato dynamicky se vyvíjející část zemského povrchu umožňuje existenci lidské civilizace napříč kontinenty v podobě, jak ji známe.

Expertní odhady hovoří o tom, že se na zeměkouli nachází přibližně 48 milionů km^2 půd využívaných pro zemědělskou činnost (Erenstein et al., 2021). Z toho přibližně zhruba 14 milionů km^2 zaujímá orná půda (Körschens, 2002; Prăvălie et al., 2021). Na těchto plochách je vyprodukována naprostá většina všech potravin. Pouze 1 % pochází z vodních zdrojů (Pimentel, 2006). Ochrana půd a jejích funkcí by tedy měla být veřejným zájmem v globálním měřítku (Clunes et al., 2022).

Ve vědecké komunitě panuje shoda, že z hlediska délky lidského života je půda přírodním zdrojem neobnovitelným (např. Gobin et al., 2004; Stefanidis et al., 2021; Brady a Weil, 2017). I přesto jsou celosvětově obrovské plochy zemědělské půdy vystaveny řadě závažných degradačních procesů, které snižují jejich bonitu (Ferreira et al., 2022). Jen ariditou je postiženo 40 % orných půd (Prăvălie et al., 2021). Mezi další iniciátory degradačních procesů se řadí například vysoká míra eroze půdy (Sanderman a Berhe, 2017) spojená se ztrátou živin (Visser et al., 2005), znečištění těžkými kovy (Vácha, 2021) či pokles obsahu organického uhlíku v půdách (Berhe et al., 2007; Smith et al., 2016).

Z hlediska zemědělství je důležitou vlastností půdy její úrodnost (Anghinoni a Vezzani, 2021; Nord et al., 2022). Definic půdní úrodnosti existuje v půdních a agronomických vědách nespočet (Patzel et al., 2000). Zjednodušeně řečeno se jedná o schopnost půdy poskytovat pěstovaným rostlinám živiny, vodu a ostatní nezbytné podmínky života po celou dobu vegetace. Je možné rozlišovat mezi úrodností potenciální a skutečnou. Potenciální úrodnost je dána přirozeným vývojem a vlastnostmi půd. Závisí na zrnitostním složení, genetickém vývoji, celkové zásobě živin v půdě atd. Z hlediska zemědělského je ovšem významnější úrodnost skutečná (efektivní). Pro ni jsou zásadní zásahy člověka do půdního ekosystému. Na úrodnost zemědělských půd mají vliv například fyzikální (zrnitostní složení, množství a poměr kapilárních a gravitačních pórů apod.) a chemické (hodnota pH, pufrační schopnost půd atd.) vlastnosti, druhové složení a početnost půdního edafonu (Moral a Rebollo, 2017), ale také množství a kvalita půdní organické hmoty (POH) (Balík et al., 2020; Cotrufo a Lavalle, 2022; Hoffland et al., 2020; Oldfield et al., 2019).

Množství organického uhlíku v půdě je již mnoho let velkým tématem nejen v souvislosti s půdní úrodností, ale též kvůli spojitosti se změnami klimatu. I přesto, že v důsledku historických změn využívání půdy a zemského pokryvu zásoba uhlíku v půdě klesla (Sanderman et al., 2017), platí, že po oceánech je pedosféra druhou největší zásobárnou uhlíku (Borrelli et al., 2018; Lugato et al., 2014). Jak uvádějí Šimek et al. (2019), vzhledem k různému původu, formě a neustálé dynamice, není přesný obsah uhlíku v půdě znám. To potvrzují rozdílná data publikovaná různými autory. Brady a Weil (2017) odhadují obsah půdního organického uhlíku na 2400 Pg, Horwath (2015) dokonce na 3051 Pg. Lal (2008) se domnívá, že zásoba organického uhlíku v půdě je 1550 Pg, dalších 950 Pg je ve formě uhličitanů. Autor také zmiňuje, že celková suchozemská biota obsahuje asi 560 Pg uhlíku a je tak hlavním zdrojem vstupů organické hmoty do půdy. Rozhodující množství půdního organického uhlíku se vyskytuje v hloubce do jednoho metru (Minasny et al., 2017; Scharlemann et al., 2014; Stockmann et al., 2013). Nejvýznamnějších je prvních 30 cm půdy (Plaza et al., 2018). V této hloubce se nachází zhruba 700 Pg organického uhlíku (Batjes, 1996).

V udržitelném zemědělství je možné dosahovat vysokých výnosů, ovšem vždy s ohledem na zachování dobrého stavu životního prostředí a blahobytu místních obyvatel (Godfray a Garnett, 2014; Pretty a Bharucha, 2014). Pro půdní úrodnost, ale i poskytování ekosystémových služeb půd, je nezbytná přítomnost POH, jež se skládá z organických sloučenin obsahujících uhlík, vodík, kyslík, dusík, síru a fosfor (Johnston et al., 2009). Je však neobyčejně složitá. Jedná se o heterogenní směs organického materiálu skládající se převážně z rostlinných, živočišných i mikrobiálních zbytků, včetně ligninů, proteinů, polysacharidů (celulóza, hemicelulóza, chitin, peptidoglykeny), lipidů, vosků, dalšího alifatického materiálu (mastné kyseliny, kutin, suberin, terpenoidy) a jiných minoritních organických látek. Zahrnuje tedy celé spektrum látek – od nerozložených rostlinných a živočišných tkání přes efemérní produkty rozkladu až po relativně stabilní a složité produkty jejich přeměn (Kolář et al., 2009).

Půdní organická hmota je esenciální součástí terestrických ekosystémů. Hraje klíčovou roli v udržení produktivity půdy a také v ochraně životního prostředí. Velmi obecně lze roli POH shrnout následovně. Má pozitivní vliv na půdní strukturu (zvyšuje se pórovitost, objemová a specifická hmotnost klesají), kapacitu zadržování vody (Sarker et al., 2022), poskytuje rostlinám živiny (N, P a S a některé mikroelementy v době vegetace a v místech půdního profilu, kde je obtížné aplikovat je hnojivy), tím že je součástí organo-minerálního koloidního komplexu půdy, zároveň podporuje i poutání živin v půdě (Gerke, 2022).

Obecně platí, že vyčerpání organického uhlíku v půdě může dramaticky ovlivnit kvalitu a zdraví půdy a následně zemědělskou produktivitu. Ztráty půdního organického uhlíku mají za následek pokles úrodnosti půdy, a proto patří mezi formy degradace půdy v globálním měřítku (Dregne, 2002; Lal, 2015; Zomer et al., 2017).

Půdy s nedostatečným množstvím (či špatnou kvalitou) POH, se vyznačují horší půdní strukturou a nižší stabilitou půdních agregátů (Darwish et al., 1995), s čímž souvisí i větší ohroženost erozí (Zhang et al., 2019). Mají menší hydraulickou vodivost, sníženou schopnost zadržovat vodu (Leroy et al., 2008), jejich schopnost poutat živiny je rovněž narušena (Lal, 2015). Dále se jedná o snížení pufrační schopnosti půd a zvýšení rizika mobility kontaminantů (Ukalska-Jaruga a Smreczak, 2020). Biologická rozmanitost půdního edafonu klesá, společně s ní i celková aktivita půdy, čímž je negativně ovlivněn i koloběh živin (Banwart et al., 2014; Pamminger et al., 2022).

2.2 Ukládání versus rozklad půdního organického uhlíku

Mezi odborníky, ale i laickou veřejností, je dlouhodobě předmětem diskuse globální změna klimatu (Abbass et al., 2022; Simpson et al., 2021). I proto je v současnosti velkým tématem ukládání organického uhlíku do půdy (Basile-Doelsch et al., 2020; Buckeridge et al., 2022; Whitmore et al., 2015). Právě v uložení atmosférického oxidu uhličitého do půdy spočívá, podle řady vědců (například Lassaletta a Aguilera, 2015; Hutchinson et al., 2007; Lal et al., 2021; Naorem, 2022; Smith, 2012), zastavení klimatických změn nebo alespoň jejich zmírnění.

V úvodu do této problematiky je třeba zdůraznit, že často dochází k záměně či směšování pojmů „sekvestrace“ a „ukládání“ organického uhlíku do půdy. Ukládání organického uhlíku znamená zvýšení jeho zásob v půdě v průběhu času na dané pozemní jednotce. Nemusí být nutně spojeno s čistým odstraněním CO_2 z atmosféry. Příkladem může být aplikace hnoje na konkrétní pole namísto jeho homogenního rozmetání po krajině. Může tak dojít k místnímu zvýšení zásob organického uhlíku v půdě, ale k odstranění CO_2 z atmosféry v měřítku krajiny dojít nemusí (Chenu et al., 2019). Sekvestrace organického uhlíku v půdě naopak předpokládá čisté odstranění atmosférického CO_2. Olson et al. (2014) definují sekvestraci uhlíku jako proces přenosu CO_2 z atmosféry do půdy prostřednictvím rostlin, rostlinných zbytků a dalších organických látek, které jsou v půdě zadržovány jako součást organické hmoty. Doba zdržení sekvestrovaného uhlíku v půdě se může pohybovat od krátkodobého až po dlouhodobé skladování (tisíciletí). Sekvestraci lze tedy kvantifikovat pro konkrétní dobu trvání. Za potenciál ukládání uhlíku dané půdní jednotky je možné označit maximální přírůstek zásob půdního organického uhlíku dosažitelný v určitém klimatu v ohraničeném časovém období. Potenciál sekvestrace uhlíku dané půdy je definován maximálním odstraněním CO_2 z atmosféry v určitém klimatu během stanoveného časového úseku.

Jakákoli podoba akumulace uhlíku v půdě má však své limity. Obsah a forma POH totiž úzce korelují s téměř všemi fyzikálními, chemickými a biologickými vlastnostmi půdy (Körschens, 2002). V žádné půdě se proto hladina POH nemůže zvyšovat donekonečna. Pro každý zemědělský systém a jeho řízení, včetně managementu organických i minerálních hnojiv, existuje rovnovážná úroveň POH. Pro stanovení vhodné úrovně rovnováhy jsou nutné dlouhodobé experimenty s nezměněnou plodinou a managementem. Dosažení významného zvýšení rovnovážné úrovně POH ve většině zemědělských systémů vyžaduje velmi velké vstupy organické hmoty. Pokud nemá obsah POH klesat, musejí být zachovány. V jakémkoli systému hospodaření bude rovnovážná úroveň v jílovité půdě vždy větší než v půdě písčité a v kterémkoli typu půdy bude vyšší u trvalých travních porostů než u dlouhodobého pěstování plodin na orné půdě. Množství organické hmoty v půdě závisí na vstupech organického materiálu, rychlosti mineralizace POH, půdní struktuře a klimatu. Tyto faktory se vzájemně ovlivňují tak, že se množství POH mění, často pomalu, směrem k rovnovážné hodnotě specifické pro daný typ půdy a systém hospodaření (Johnston et al., 2009). V posledních staletích obsah uhlíku v půdách často klesal, a to zejména v půdách obdělávaných. Proto Wander a Nissen (2004) uvádějí, že by sekvestrace uhlíku neměla být chápána jako uložení nového uhlíku do půdy, ale jako znovuobnovení původních zásob.

Nelze opomenout, že jedním z obecně uznávaných indikátorů „půdního zdraví“ je půdní respirace (Bongiorno et al., 2019; Cardoso et al., 2013; Nunes et al., 2020). Čím je půdní edafon aktivnější, tím větší přínosy POH jsou. Z hlediska zemědělské produkce tedy výhody organické hmoty nevyplývají z její akumulace, ale z jejího rozkladu (Janzen, 2006). Relativně labilní frakce POH (mineralizují v rámci měsíců až let) jsou proto zásadní z hlediska úrodnosti půdy. Nejen že jsou zdrojem energie pro půdní organismy, ale po svém rozkladu poskytují potřebné živiny také rostlinám (Bongiorno et al., 2019; Körschens, 2002). Pro zemědělskou produkci na orné půdě tedy není stěžejní absolutní hodnota množství organického uhlíku v půdě, ale naopak intenzita rozkladu organické hmoty.

Z výše uvedeného je tedy jasné, že organická hmota v půdě je mnohem více než jen potenciální nádrž pro zadržování přebytečného CO_2. Popisovanou problematiku je tedy možné shrnout slovy Janzen (2006). Autor jednoznačně uznává, že sekvestrace uhlíku je chvályhodný a rozumný cíl. Zmiňuje, že řada autorů sekvestraci vnímá jako „win-win“ řešení. Nejenže odstraňuje nadbytečný CO_2 z atmosféry, ale zároveň zlepšuje půdu tím, že přidává do půdy organickou hmotu, což je zdroj energie a živin pro biotu. Současně však důrazně upozorňuje na často přehlížený rozpor, který s ukládáním uhlíku do půdy nepochybně souvisí, a to, jak zvýšit zásobu organického uhlíku v půdě a současně zachovat její biologickou aktivitu? S konstantními vstupy uhlíku totiž není možné současně podpořit mikrobiální aktivitu a zároveň zvýšit obsah půdního organického uhlíku. Snížení biodiverzity půd a utlumení aktivity edafonu by vedlo k potlačení mnoha ekosystémových funkcí (Dominati et al., 2010; Hooper et al., 2012; Lori et al., 2017; Philippot et al., 2013; Schmidt et al., 2011). V zásadě je tedy možné buď podporovat mikrobiální aktivitu a „obětovat“ půdní uhlík, nebo uložit do půdy více uhlíku na úkor mikrobiální aktivity. Z uvedeného textu tedy vyplývá, že při prosazování sekvestrace C v orných půdách se sledují dva protichůdné cíle: ukládání organické hmoty a zároveň její rozklad. Výzkumníci by tedy neměli pouze hledat cesty, jak do půdy uložit co nejvíce uhlíku. Skutečnou metou vědeckého bádání by mělo být nalezení optimální rovnováhy mezi zásobami a spotřebou organického uhlíku, které jsou v daném období pro vybraný ekosystém a jeho služby nejpříznivější.

2.3 Perzistence půdní organické hmoty

Půdní organická hmota není v žádném případě soubor biochemicky nebo kineticky jednotných molekul (Guigue et al., 2022). Právě kvůli vysoké heterogenitě této skupiny látek bylo zavedeno hodnocení POH prostřednictvím celkového obsahu organického uhlíku. Někteří autoři uvádějí, že vynásobí-li se obsah C (%) koeficientem 1,724, výsledkem je procentuální množství organické hmoty v půdě (např. Johnston et al., 2009). Řada autorů dokonce výsledný součin nepovažuje za obsah organické hmoty, ale označuje ho přímo za množství humusu. Například Körschens (2021) uvádí tuto rovnici: humus = půdní organická hmota = živé a mrtvé organické substance v půdě = organický uhlík·1,724 (a to i přesto, že ve své práci z roku 2002 na nesprávnost násobícího koeficientu 1,724 upozorňuje).

Pouhé stanovení celkového organického uhlíku v půdě totiž nevypovídá nic o kvalitě POH, ani jejím charakteru (Kolář a Lošák, 2023). Používání násobícího faktoru 1,724 (které se dodnes ve výzkumných pracích objevuje) je také naprosto chybné (například Bierer et al., 2021; Minasny et al., 2020, Pribyl, 2010). Jak bylo již několikrát zmíněno, POH je velice heterogenní směs, jejíž složky mají rozličné vlastnosti. Proto řada autorů POH dělí do různých skupin.

I Körschens (2021), který stále využívá koeficientu 1,724 a nerozlišuje mezi humusem a POH, nabádá ke striktnímu rozdělení organické hmoty do dvou skupin. Odděluje humus trvalý, který se neúčastní mineralizačních procesů, a humus živný, jež je více méně rozložitelný. Podobně, ovšem přesněji, rozlišuje Stevenson (1994) zvlášť lehkou frakci a frakci označenou jako humus. Za humus považuje huminové látky a produkty syntetizované mikroorganismy, které se stabilizovaly jako nedílná součást půdy. Johnston et al. (2009) uvádějí, že humus neobsahuje žádnou stopu po anatomické struktuře materiálu, ze kterého byl odvozen.

Hayes a Swift (1978) popisují POH jako heterogenní směs všech organických složek nacházejících se v půdě. Rozdělují jí do dvou skupin s různými morfologickými a chemickými vlastnostmi. Do první skupiny patří čerstvé organické zbytky a netransformované součásti starších rozkládajících se látek. Druhá skupina zahrnuje transformované produkty (nazývané humus), které nemají žádnou morfologickou podobnost se strukturami, ze kterých byly odvozeny. Tyto transformované komponenty označují jako humifikované produkty. Skládají se ze zhumifikovaných i nezhumifikovaných substancí a lze je proto dále dělit. Jednou podskupinou jsou amorfní, hnědě zbarvené huminové složky (huminové kyseliny, fulvokyseliny, huminy). Do druhé podskupiny se řadí další látky patřící do rozpoznatelných tříd, jako jsou například polysacharidy, polypeptidy, pozměněné ligniny atd.

Kolář et al. (2005) navrhují POH rozdělovat také na dvě skupiny. První z nich označuje jako primární půdní organickou hmotu (PPOH). Do této kategorie řadí veškerou POH, která neprošla celým procesem humifikace. I když má různou stabilitu v procesech hydrolýzy a oxidace, tedy i různou rychlost biodegradability, je z hlediska časového úseku jednotek a desítek let rozložitelná. Může mít i značnou sorpční kapacitu, ale vždy nízkou kationtovou výměnnou kapacitu (KVK). Druhou skupinou je ta část POH, která prošla celým procesem humifikace. Tuto část POH Kolář et al. (2005) označují jako humus. Na rozdíl od PPOH má výraznou nejen sorpční kapacitu, ale také KVK. Humus považují za stabilní organickou frakci, která je rozložitelná v časovém úseku stovek až tisíců let.

Citovaní autoři vycházejí z tradičních frakcionačních postupů, jimž předchází alkalická extrakce humusových látek. Předpokládají, že procesem humifikace vznikají polymerní makromolekulární huminové látky, které jsou odolné vůči rozkladu díky své přirozené chemické stabilitě. Ta je dána jejich neuspořádanou makromolekulární strukturou (Almendros a Dorado, 1999) a je ovlivněna také molekulovou hmotností (Wei et al., 2014). Proto obecně platí, že fulvokyseliny jsou rychleji mineralizovatelné než huminové kyseliny (Qualls, 2004). Humifikační model, který uznává přítomnost a stabilitu huminových látek v půdě, byl vědci uznáván více než 200 let (Olk et al., 2019).

V posledních letech je ovšem humifikační model některými autory zpochybňován. Pochyby o správnosti humifikačního modelu publikovali již v roce 2010 Kleber a Johnson (2010). Schmidt et al. (2011) uvedli, že stabilita organické hmoty není určena její molekulární strukturou, ale je dána funkcí půdních vlastností a prostředí. Lehmann a Kleber (2015) zažitou koncepci dělení POH zásadně odmítají. V jejich článku dokonce popírají tvorbu, a snad i existenci, huminových látek. Domnívají se, že huminové látky nejsou v půdě přítomny (alespoň v takové formě jako po jejich izolaci) a vznikají během alkalické extrakce POH (Kleber a Lehmann, 2019). Lehmann a Kleber (2015) představili tzv. model půdního kontinua. Půdní organickou hmotu tak považují za kontinuum progresivně se rozkládajících organických sloučenin (od původních vstupů neporušené biomasy po vysoce oxidovaný uhlík karboxylových kyselin). Organické fragmenty jsou tedy nepřetržitě zpracovávány komunitou rozkladačů od velkých rostlinných a živočišných zbytků směrem k menší velikosti molekul. Větší oxidace organických materiálů zvyšuje rozpustnost ve vodě a zároveň poskytuje příležitost k ochraně proti dalšímu rozkladu spojením s minerálními povrchy a zabudováním do agregátů. Tento model se tedy soustředí na schopnost rozkladačů získat přístup k POH a na ochranu, kterou poskytuje minerální složka půdy organické hmotě. Předpoklad výskytu zhumifikovaných látek a jejich odolnost vůči biodegradabilitě jsou popírány.

Ačkoli je model půdního kontinua v současnosti velmi diskutovaným tématem a článek The contentious nature of soil organic matter, který jej popisuje, má na Web of Science přes 1 700 citací, objevilo se množství autorů, kteří nejsou přesvědčeni o jeho správnosti. Naopak patří mezi zastánce teorií vycházejících z humifikačního modelu. Rozsáhlou práci poukazující na slabá místa modelu půdního kontinua publikovali Hayes a Swift (2020). Poukazují na jejich chybné předpoklady a dezinterpretace, zaujatost, neschopnost citovat články, které jsou v rozporu s jejich názory. Zároveň jsou přesvědčeni, že model půdního kontinua není dostatečně podepřen reálnými experimenty, zejména z oblasti pedochemie. Dalšími významnými kritiky jsou například De Nobili et al. (2020) či Olk et al. (2019).

3 Komentované publikace autora – Část 1

Tato část habilitační práce obsahuje tři studie, které se přímo zabývají organickou hmotou v půdě a jejím hodnocením. První článek se týká dělení půdní organické hmoty podle její stability vůči oxidaci a navrhuje novou metodu pro hodnocení POH. V druhém článku je pozornost zaměřena na labilní frakce půdní organické hmoty. Organická hmota a půdní struktura byla sledována při pěstování kukuřice seté různými technologiemi. Byly hledány optimální indikátory, které jsou schopny zachytit změny labilních frakcí i během krátké doby. Poslední článek z této skupiny je zaměřen naopak na stabilní část POH, konkrétně na tzv. black carbon. V literatuře se často objevují zmínky o jeho vysoké stabilitě, a tedy i schopnosti sekvestrovat uhlík. Bylo zjištěno, že v půdách se objevují dva typy této formy POH. Jedná se o black carbon, který vznikl v dávné historii při požárech vegetace a o black carbon antropogenní, který je spojen s lidskou činností (spalovací procesy). Tento „nový“ antropogenní black carbon není významně stabilizován koloidní minerální frakcí. Lze se tedy domnívat, že jeho odolnost vůči mineralizaci bude nižší v porovnání s black carbonem historickým.

Publikace 1: Dělení půdní organické hmoty na labilní a stabilní frakce

Kopecký, M., Kolář, L., Perná, K., Váchalová, R., Mráz, P., Konvalina, P., ... & Dumbrovský, M. (2022). Fractionation of Soil Organic matter into Labile and Stable Fractions. *Agronomy, 12*(11), 73. DOI: 10.3390/agronomy12010073.

Z výše uvedeného textu vyplývá, že terminologie v oblasti hodnocení POH je velmi nejednotná. Srovnávání dat publikovaných různými autory je proto často velice obtížné. Zmíněné problematice se částečně věnuje i tento článek. Především je nutné přijmout fakt, že organická hmota v půdě je velmi pestrou směsí látek. Je tedy zřejmé, že v různých zemědělských půdách může mít POH odlišné vlastnosti, a to třeba i velmi výrazně. Množství organické hmoty tak nevypovídá nic o její kvalitě. I samotné hodnocení obsahu POH je zavádějící. Například Körschens (2002) uvádí, že 0,8 % organického uhlíku v písčité půdě by mohlo být považováno za lepší výsledek než 1,5 % organického uhlíku v černozemi. Je tedy vždy nutné brát v potaz místní podmínky.

V kapitole 2.3 je nastíněna aktuální problematika povahy POH. Je řešen rozpor mezi desetiletími zavedeným úzusem vysoké stability huminových látek (především huminových kyselin) a modelem půdního kontinua, který předpokládá, že veškeré organické látky se v půdě rychleji či pomaleji přeměňují na menší a menší částice a stabilita huminových kyselin je zpochybňována.

Tento článek se věnuje ověření nové metody hodnocení POH, která není v přímém rozporu ani s modelem humifikace, ani modelem půdního kontinua. Organická hmota je zde dělena na tzv. primární půdní organickou hmotu (PPOH) a stabilní frakce organické hmoty, a to na základě jejich odolnosti vůči oxidaci. Pro půdní úrodnost jsou cenné především labilní frakce POH (Bayer et al., 2002; Haynes, 2005), které jsou reprezentovány PPOH. Hodnota této frakce spočívá v jejím relativně rychlém rozkladu. Díky své labilitě tedy slouží jako zdroj energie pro půdní mikroorganismy. Následně, po procesu mineralizace, uvolňuje živiny rostlinám. Za druhou skupinu organické hmoty je považována ta, jež za daných podmínek (0,4 mol/l roztok $K_2Cr_2O_7$ v 12M H_2SO_4 při 90 °C po dobu 30 min) nezoxiduje. Je označována jako stabilní organická frakce. Protože tyto relativně stabilní frakce za daných laboratorních podmínek nezoxidují, je možné předpokládat, že jejich stabilita bude oproti stabilitě PPOH vyšší i v reálných půdních podmínkách. Avšak i tyto stabilní frakce mají v půdě svou funkci. Je zřejmé, že do stabilní frakce spadají i látky, které díky svým záporně nabitým zbytkům funkčních skupin –COOH a fenolických –OH skupin s oddisociovatelným vodíkem mohou být nejen půdním ionexem, ale spolu s aktivními povrchovými silami i donorem vazby s koloidní minerální půdní frakcí. Tím pomáhají tvořit půdní strukturu a ovlivňují tak fyzikální vlastnosti půdy včetně vodního a vzdušného režimu (Kolář et al., 2017). Dalším benefitem těchto látek je jejich vysoká schopnost kationtové výměny (Váchalová et al., 2014). Nelze opomenout ani fakt, že po časově omezenou dobu zůstává uhlík fixován v půdním prostředí.

Metoda umožňuje nejen stanovit obsahy (vyjádřené organickým uhlíkem, který jim náleží) obou skupin, ale hodnotí i jejich kvalitu. Kationtová výměnná kapacita vyjadřuje kvalitu stabilní organické frakce. Kvalita PPOH je vyjádřena rychlostní konstantou oxidace PPOH prostřednictvím 0,4 mol/l roztoku $K_2Cr_2O_7$ v 12M H_2SO_4 při 60 °C během 40 minut.

Tato metoda je určena pro zemědělskou praxi, nikoli pro hlubší vědecký výzkum. Zemědělcům by měla poskytnout informace o stavu POH, které jim pomohou při rozhodování, zda použít více či méně rychle mineralizující hnojiva (například kejda nebo zelené hnojení) nebo hnojiva se stabilizovanější organickou hmotou, jako je hnůj, kompost, nebo dokonce digestát z bioplynové stanice. Zemědělci, kteří mají podrobné informace o kvalitě POH, se tak mohou správně rozhodnout o využití různých agrotechnických opatření ke zvýšení mikrobiální aktivity půdy, která je pro zlepšení úrodnosti půdy zásadní.

Práce si kladla za cíl porovnat klasické metody (stanovení obsahu huminových kyselin a fulvokyselin, jejich poměr $C_{HK}:C_{FK}$ a barevný kvocient $E_{4/6}$) s touto novou metodu při hodnocení POH. Byla zkoumána hypotéza, že klasické postupy lze nahradit novou metodou, která je relativně levná, jednoduchá a přístrojově nenáročná.

Klasické metody, které jsou založené na izolaci huminových látek alkalickou extrakcí půdního vzorku a vysrážením huminových kyselin z extraktu v kyselém prostředí jsou autory Lehmann a Kleber (2015) kritizovány. Ačkoli nová metoda nepracuje s extrahovanými huminovými kyselinami, má také svá „slabá místa“. Jde například o to, že chemická oxidace je pouze simulací procesu biodegradace v přírodních podmínkách. Stejně tak ne všechny látky, které spadají do stabilní organické frakce, mají pozitivní vliv na půdní strukturu či zvyšování kationtové výměnné kapacity.

V pokusu bylo analyzováno šest půdních vzorků. Výsledky ukázaly, že to, co bylo běžně považováno za obsah humusu – součet uhlíku huminových kyselin a fulvokyselin, je možné nahradit stanovením obsahu stabilních organických frakcí. Naopak bylo zjištěno, že výsledky stanovení kationtové výměnné kapacity nelze podle statistického vyhodnocení považovat za rovnocennou náhradu zavedeného hodnocení, kdy je počítán poměr $C_{HK}:C_{FK}$. Přesto je kationtová výměnná kapacita dobrým indikátorem kvality půdy (Khaledian et al., 2017; Taghizadeh-Mehrjardi, 2016).

Nově ověřovaná metoda však oproti klasickým postupům umožňuje hodnocení kvality PPOH prostřednictvím rychlostní konstanty její oxidace. Získané výsledky poskytují jasnou informaci o stavu POH. Důmyslným používáním vhodných organických hnojiv mohou zemědělci zlepšit podstatné vlastnosti půdy, včetně její úrodnosti.

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Fractionation of Soil Organic Matter into Labile and Stable Fractions

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Abstract: The present study aims to test and evaluate the efficiency of a new modified method of organic matter evaluation. It allows the assessment of the quality and quantity of the primary soil organic matter and the stable organic fractions separately. The new method was tested in six soil samples of different localities in the Czech Republic. This method is based on observing reaction kinetics during the oxidation of soil organic matter and measuring the cation-exchange capacity of stable organic fractions. The results were compared with classical methods, which rely on the isolation of humic substances, determination of the content of humic acids and fulvic acids and their ratio C_{HA}:C_{FA}, quotient $E_{4/6}$, and fractionation of soil organic matter according to resistance to oxidation. It turned out that the results of the new modified method are more sensitive in comparison with the results obtained by classical procedures. The linear regression demonstrated the dependence between the amounts of soil organic matter determined by the classical method compared with the modified method. Moreover, the new modified method was found to be faster and not demanding on laboratory equipment. The new method has been improved to be easily repeatable, and some shortcomings of the previous method were eliminated. Based on our results and other recent studies, the modified method may be recommended for the practical evaluation of soil organic matter conditions.

Keywords: analytical methods; fractionation; lability; modified method; soil organic matter; stability

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1. Introduction

Soil terrestrial ecosystems are a significant producer of food for humans, livestock feed, as well as a source of phytomass for energy purposes [1,2]. In recent years, many studies have pointed to the deteriorating quality of agricultural soils. Due to the growing worldwide population and deteriorating environment, an ever-increasing pressure is exerted on the production properties of the soils. Thus, the quality of agricultural soils is an increasingly actual topic [3–6].

Soil organic matter (SOM) is one of the most important factors determining soil fertility. Many previous studies have repeatedly shown the irreplaceable role of SOM. Soils with insufficient SOM are characterized by poor structure and low stability of aggregates [7,8]; they have low hydraulic conductivity and water-holding capacity [9], and generally low nutrient-binding capacity [4]. Moreover, the important roles of SOM in acid buffering were found [10]. The amount of organic carbon in the soil is also important in terms of its temporary storage in the soil. Small changes in the soil organic carbon stock could result in significant impacts on the atmospheric carbon concentration [11].

The adequate use of organic fertilizers is one measure leading to an increase in the amount of the SOM in the agricultural soils [12], which can increase microbial activity [13]. High microbial activity is one of the foundations of potential soil fertility [14]. However, the effect of organic fertilization depends not only on the quantity but also on the quality of the fertilizer used and the environmental conditions [15]. Moreover, farming methods (fertilization, tillage, irrigation, etc.) can affect the decomposition of organic matter [16,17]. For example, Li et al. [18] found that N fertilization decreases SOM decomposition and increases the efficiency of C sequestration in the soil through a higher portion of undecomposed crop residues.

The high content of total organic carbon (TOC) is often highlighted in the literature as a sign of soil quality [19]. However, the amount of TOC is unequal to the SOM quality. Thus, it is evident that the amount of TOC in the soil cannot indicate the quality of SOM. Moreover, the farmers usually do not even distinguish between labile and stable forms of organic fertilizers and other sources of SOM.

In general, the less stable the organic matter, the more it contributes to soil fertility. Therefore, many authors consider the content of the labile fraction of SOM as a sign of potential soil fertility [16,20–22]. However, not only the labile fractions of SOM are important. The stable fractions, mainly due to their cation-exchange capacity (CEC) and the positive effect on soil structure (especially humic acid), are also essential [23,24]. Cation-exchange capacity is one of the most critical soil properties to measure soil ability to bind and hold positively charged ions [25,26].

However, the boundary between labile and stable organic matter is ambiguous. Many authors fractionate organic matter differently [20–24,27,28]. However, undoubtedly hot water extractable carbon can be considered labile [29]. From the point of view of stability, the opposite side is represented by black carbon [30]. The boundary between labile and stable SOM is given by resisting oxidation in the present study. The part of SOM which resists oxidation in a 0.4 mol/L solution of $K_2Cr_2O_7$ in 12 M of H_2SO_4 at 90 °C for 30 min is considered stable.

Maroušek et al. [31] published a new analytical method that is relatively not demanding on laboratory equipment. In our work, we used the principle of this method to evaluate the quality and quantity of organic matter in soil samples. However, we proceeded to a slight modification. We used this method to evaluate three forest soil samples and three arable land samples. We also evaluated these samples by classical methods (determination of the content of humic acids and fulvic acids, their ratio C_{HA}:C_{FA} and the quotient $E_{4/6}$).

The work aimed to compare classical and modified methods in terms of their effectiveness of sample evaluations according to the quality and quantity of SOM. The hypothesis that classical procedures could be replaced by the modified method was examined, which is undemanding in terms of instrumentation and brings results useful in agricultural practice.

2. Materials and Methods

2.1. Samples Used

Six soil samples from forest and agricultural land of the Czech Republic were tested using both the classical method (CM) and the newly modified method (MM), described by Maroušek et al. [31].

Soil samples were as follows (soil taxonomy according to the World reference base for soil resources 2014 [32]):

A: Borová Lada locality at an altitude of 895 m, GPS coordinates: 48.986409, 13.671749; forest soil sample (O-horizon) of medium-heavy cambisols (forest composition: spruce 65%, pine 21%, birch 10%);

B: Zahrádky near Borová Lada locality at an altitude of 880 m, GPS coordinates: 48.977437, 13.689511; forest soil sample (O-horizon) of medium-heavy gleysols (forest composition: spruce 81%, beech 11%, pine 4%);

C: Plavsko near Stráž and Nežárkou locality at an altitude of 464 m, GPS coordinates: 49.088498, 14.894712; forest soil sample (O-horizon) of medium-heavy stagnosols (forest composition: pine 79%, spruce 13%, oak 4%);
D: Opařany locality at an altitude of 465 m, GPS coordinates: 49.405163, 14.478683; agricultural soil sample (A-horizon) of medium-heavy cambisols;
E: Třeboň locality at an altitude of 434 m, GPS coordinates: 49.023263, 14.647633; agricultural soil sample (A-horizon) of medium-heavy luvisols;
F: Modřice u Brna locality at an altitude of 204 m, GPS coordinates: 49.115030, 16.614573; agricultural soil sample (A-horizon) of medium-heavy chernozems.

One composited soil sample was taken from each locality. The first group of samples (A, B, C) includes typical forest soils of the Czech Republic. Forest soils were chosen because significant differences in the quantity and quality of their organic matter could be expected. There was a presumption that these differences should be measurable by all methods and therefore clearly evaluable. This is important for illustration of the obtained results. The second group of samples (D, E, F) includes arable lands, represented by typical soil types of the Czech Republic. Sampling was performed using a pedological sampling rod in May 2020.

Twenty subsamples (diagonally across the forest/field) were taken from each locality and composited. Material from the composited samples was used for subsequent processes. The depth of sampling depended on the thickness of the soil horizon in the forest. The depth of sampling was 0–0.2 m on the arable lands. Samples were dried at 60 °C to constant weight. Particles larger than 2 mm were removed from the samples. The remaining soil was homogenized and sieved through a 0.25 mm sieve. The analysis was made using the resulting fine-grained soil.

The total organic carbon content of the samples was determined using the equipment Primacs SLC Analyzer (SKALAR, Netherlands) with a dual-oven design, allowing separate analysis of total carbon (TC) and inoragnic carbon (IC). Total carbon is determined by catalytic oxidation of the sample at 1100 °C, converting the carbon present in the sample to CO_2, which is detected by the nondispersive infrared detector. Inorganic carbon is determined by acidification of the sample in the IC reactor, which converts the inorganic carbon to CO_2. TC−IC = TOC.

The procedure for performing other analyses is described below. Each analysis was repeated six times for each individual sample.

2.2. Classical Method (CM)

The amount of carbon that belongs to humic acids (C_{HA}) and the amount of carbon that belongs to fulvic acids (C_{FA}) can be determined by the classical method. The sum of these values (C_{HA+FA}) indicates the amount of humic substances. The quality of humic substances is derived from the C_{HA}:C_{FA} or the quotient $E_{4/6}$. It is also possible to determine the amount of non-humidified SOM which has been designated as primary soil organic matter (PSOM). The carbon belonging to this fraction (C_{PSOM}) can be determined by subtracting C_{HA} and C_{FA} from the TOC value. The degree of stability of the SOM is determined by fractionation according to resistance to oxidizing [28].

The humic substance content and the C_{HA}:C_{FA} were determined as follows: The soil samples were extracted in a Soxhlet extractor with a mixture of ethanol and benzene to remove soil bitumens (5 h). After drying, five grams of treated soil were used for the analysis. This was poured over with 100 mL of a 0.1 mol/L mixture of sodium pyrophosphate and sodium hydroxide (44.6 g $Na_4P_2O_7 \cdot 10\ H_2O$ + 4 g NaOH was dissolved in distilled water made up to 1000 mL). After 12 h of extraction in a rotary shaker, the mixture was filtered. In addition, 200 mL of the extract was pipetted and precipitated with concentrated H_2SO_4 (98.08 g/mol) until turbidity appeared. After mixing, the precipitated extract was placed in a thermostat at 65 °C for 30 min. It was subsequently stored at 20 °C for 12 h. After filtering the humic acids and washing them with 0.1 mol/L H_2SO_4, the coagulated humic acid was dissolved with 0.05 mol/L NaOH. The C_{HA} content was determined in dissolved

C_{HA} gel. The C_{FA} carbon was determined in the filtrate after filtration of the humic acids. Subtraction of these two values from the TOC in the sample revealed the C_{PSOM} content.

The determination of the color quotient $E_{4/6}$ was performed after the decalcination of the samples with 0.2 mol/L H_2SO_4. In addition, 30 mL of 0.1 mol/L NaOH was added to 2 g of the decalcinated sample and allowed to stand for 24 h. Then, 5 mL of saturated Na_2SO_4 solution was added and immediately centrifuged. The soil was washed with a 0.01 mol/L NaOH until the supernatant was clear. The solution was made up to 500 mL with distilled water. Humic acids were precipitated from a total volume of 0.1 mol/L H_2SO_4, centrifuged, and washed with distilled water. The humic acid precipitate was then dissolved in 50 mL of 0.02 mol/L $NaHCO_3$. The solution was adjusted to contain 13.6 mg of C in 100 mL with distilled water. Solution extinction measurement (Spectrophotometer Perkin Elmer model Lambda 15 UV–Vis) was then carried out at two wavelengths, and the color quotient $E_{4/6}$ was determined: E_{465}/E_{619}.

Determination of the degree of stability of SOM in CM was performed by fractionating into four groups according to carbon content after oxidation with $K_2Cr_2O_7$ solution (Chan et al. method [28]). Only the H_2SO_4 concentration was adjusted. Treated samples were weighted into three flasks in the amount of 0.25 g. Another three flasks were free of samples (blank samples). Five mL of $K_2Cr_2O_7$ solution was added to these six flasks. Five mL of concentrated H_2SO_4 (98.08 g/mol) diluted in distilled water was added to one flask with the sample and one without the sample in an acid:water ratio of 0.5:1. Five mL of concentrated H_2SO_4 diluted in water was added to the second flask with the sample and the second one without the sample in a ratio of 1:1. Five mL of concentrated H_2SO_4 diluted in water was added to a third flask with the sample and a third one without the sample in a ratio of 2:1. All flasks were placed into a thermostat at 125 °C for 5 min. After cooling, the amount of residual $K_2Cr_2O_7$ was determined in all flasks by titration with $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ solution (automatic titrator DL 50 Mettler-Toledo, Greifensee, Switzerland). The oxidized carbon content of the first flask after a subtraction blank test corresponds to the carbon of the labile organic substances, the oxidized carbon content of the second flask corresponds to the carbon of the semi-labile organic substances, and the oxidized carbon content of the third flask corresponds to the carbon of the fraction of semi-stable substances. The fraction of the stable substances was calculated by subtracting the carbon of the semi-stable substances from the TOC.

2.3. Modified Method (MM)

The PSOM fraction and the stable organic fractions (SOF; the carbon belonging to SOF is indicated as C_{SOF}) were evaluated separately. This allowed us to determine not only their quantity but also their quality. The quality of PSOM was evaluated according to its oxidation speed constant *k*. The quality of SOF was expressed in terms of their CEC.

The principle of this method is described by Maroušek [31]. Therefore, a procedure will be described below simplified.

2.3.1. Quality of Primary Soil Organic Matter

It was necessary to determine the kinetics of the oxidation of soil carbon. The soil samples (5 flasks for one soil sample) were dispersed in a solution of 0.4 mol/L of $K_2Cr_2O_7$ in 12 M of H_2SO_4. Their organic substances were oxidized at the temperature of 60 °C in a water bath. During this time, four partial samples were taken out gradually in 10 min, 20 min, 30 min, and 40 min. Then, the amount of oxidizable carbon (C_{OX}) was determined (automatic titrator DL 50 Mettler-Toledo, Greifensee, Switzerland) in the samples. From the measured values, we calculated the speed constant of oxidation (it was the 1st order reaction). Then, the temperature was raised to 90 °C and, after 30 min, C_{OX} was determined in the sample from the last flask and was designated as C_{PSOM}.

Calculation of the speed constant *k* for oxidation of PSOM of a soil sample was the following: five sub-samples were collected at intervals of 10 to 40 min, and the C_{OX}, which may be designated as C_{OX1} to C_{OX4}, was determined. These samples were determined during the oxidation at 60 °C. C_{PSOM} value was known from the end of the determination at 90 °C (30 min). It follows the calculation of the differences of the detected values: C_{PSOM}–C_{OX1}, C_{PSOM}–C_{OX2}, C_{PSOM}–C_{OX3}, C_{PSOM}–C_{OX4}. The logarithms of these differences were determined. These logarithms were recorded in the right coordinate system on the *y*-axis versus time in minutes on the *x*-axis. Because tg α is the ratio between the opposite and adjacent leg of a right-angled triangle, whose hypotenuse is a recorded trend line, the calculation of the constant *k* is 2.303 times that ratio and has the dimension (min). For clarity, we presented the results in seconds. The higher the value, the more labile PSOM is and therefore of better quality in terms of its main function in the soil (energy source for soil organisms and nutrient source for crops).

2.3.2. Calculation of the Amounts of C_{PSOM} and C_{SOF}

The value C_{PSOM} is a measure of the quantity of the PSOM. In given conditions, stable organic fractions (especially humic acids) do not take part in the oxidation in a solution of 0.4 mol/L of $K_2Cr_2O_7$ in 12 M of H_2SO_4. If TOC in a soil sample is determined, the difference between TOC and C_{PSOM} is the amount of C_{SOF}.

2.3.3. Determination of Quality of Stable Organic Fraction

In the MM, we derive the quality of SOF from their CEC. The PSOM may also have a quite high sorption capacity, but its CEC compared to HA is negligible. The cation-exchange capacity of SOF can be determined by conductometric titration with a volumetric solution of $Ba(OH)_2$. However, the CEC value of the mineral portion of the soil sample must be subtracted. First, the CEC of the soil sample is determined, then the SOM is oxidized with hydrogen peroxide (15%) in acetic acid. The difference in results after re-determination of the CEC corresponds to the CEC of the mineral portion of the soil sample.

2.4. Statistical Analysis

The data of tables were statistically evaluated by an analysis of variance (ANOVA), and the results were subsequently compared by a post-hoc Tukey HSD test (Statistica 14.0 software, TIBCO Software, Inc., Palo Alto, CA, USA, 2021). Linear regression was performed using the QC Expert 3.3 Pro (TriloByte Statistical Software Ltd., Pardubice, Czech Republic), and the NCSS 2019 Statistical Software (NCSS, LLC., Kaysville, UT, USA). The graphical outputs of linear regression were performed using the Statistica 14.0 software. Linear regression modelling used the regression triplet [33] and consisted of the following steps: (1) model design, (2) preliminary data analysis (multicollinearity, heteroskedasticity, autocorrelation and influence points), (3) estimation of parameters using the classical least squares method (LSM) and subsequent testing of the significance of parameters using the Student's *t*-test, mean square error of prediction, and Akaike information criterion (AIC), (4) regression diagnostics—identification of influence points and verification of the LSM assumptions, and (5) construction of the refined model [33]. Statistical significance was tested at a significance level of $p = 0.05$. The methods of principal component analysis (PCA) and factor analysis [33] were used for multivariate statistical analysis of the measured data.

3. Results

3.1. Fractionation According to the Carbon Content

It is apparent from Table 1 that the most of the TOC was in sample B ($F_{(5,\,30)} = 120{,}100$; $p < 0.00001$). Table 1 further shows the C_{PSOM} and C_{HA}+$_{FA}$ fraction content according to CM and the C_{PSOM} and C_{SOF} fraction content according to the MM. The amount of C_{SOF} was statistically different in the majority of samples (D equal E) according to the MM ($F_{(5,\,30)} = 3553.6$; $p < 0.00001$). According to CM, C_{HA+FA} was possible to differ for only four groups ($F_{(5,\,30)} = 1926.9$; $p < 0.00001$). According to both methods, the content of stable fractions was the lowest in samples D and E. It is evident that the higher C_{PSOM} content was determined with the MM. However, it was found that the order of samples according to the values corresponded to CM.

Table 1. Soil carbon fractionation of samples A, B, C, D, E, F according to Classical method (CM) and Modified method (MM) (±SD).

Parameter	Method	Sample					
		A	**B**	**C**	**D**	**E**	**F**
TOC	C-Analyzer	13.61 ± 0.08^{d}	16.51 ± 0.08^{f}	14.82 ± 0.05^{e}	1.40 ± 0.02^{b}	0.90 ± 0.01^{a}	3.70 ± 0.02^{c}
C_{PSOM}	CM	$9.50 \pm 0.17^{e}_{a}$	$12.38 \pm 0.21^{f}_{a}$	$8.28 \pm 0.17^{d}_{a}$	$1.02 \pm 0.12^{b}_{a}$	$0.69 \pm 0.07^{a}_{a}$	$2.93 \pm 0.08^{c}_{a}$
C_{PSOM}	MM	$10.67 \pm 0.07^{e}_{b}$	$14.27 \pm 0.11^{f}_{b}$	$10.37 \pm 0.10^{d}_{b}$	$1.22 \pm 0.02^{b}_{b}$	$0.79 \pm 0.02^{a}_{b}$	$3.26 \pm 0.04^{c}_{b}$
C_{HA+FA}	CM	$4.11 \pm 0.15^{c}_{b}$	$4.13 \pm 0.21^{c}_{b}$	$6.54 \pm 0.18^{d}_{b}$	$0.39 \pm 0.14^{a}_{b}$	$0.22 \pm 0.07^{a}_{b}$	$0.77 \pm 0.09^{b}_{b}$
C_{SOF}	MM	$2.93 \pm 0.04^{d}_{a}$	$2.24 \pm 0.13^{c}_{a}$	$4.45 \pm 0.11^{e}_{a}$	$0.18 \pm 0.02^{a}_{a}$	$0.11 \pm 0.03^{a}_{a}$	$0.44 \pm 0.06^{b}_{a}$

Note: TOC—total organic carbon (%); C_{PSOM}—the carbon belonging to primary soil organic matter (%); C_{HA+FA}—the carbon belonging to humic acids and fulvic acids (%); C_{SOF}—the carbon belonging to stable organic fractions (%); significant differences between samples within parameters are shown in upper case letters (Tukey's honest significance test; $p = 0.05$); significant differences between methods within samples are shown in lower case letters (Tukey's honest significance test; $p = 0.05$).

A statistically significant linear regression dependence between C_{PSOM} contents determined by CM and MM was demonstrated (data from all six localities). The equation of the straight line relating C_{PSOM} MM and C_{PSOM} CM is estimated as: C_{PSOM} MM = (0.0335) + (1.1612) C_{PSOM} CM using the 36 observations in this dataset. The statistical characteristics of the regression are as follows: R = 0.9974, $R^2 = 0.9948$, MEP = 0.1541, AIC = −66.4542. The model is significant according to the Fisher–Snedecor model significance test (F = 6516.7399, quantile F = 4.1300, $p = 1.9601 \times 10^{-40}$). The model shows multicollinearity (M_T) according to Scott's criterion of multicollinearity (SC = 0.3333, M_T is at the lower end of the test $M_T < 0.33$, the model is not significantly affected by multicollinearity, and therefore there is no need to modify the model [33]). The assumption of homoscedasticity for residuals was validated (Cook–Weisberg test). Residuals do not have a normal distribution (Jarque–Bera Test). Residuals are positively autocorrelated (Durbin–Watson test) (Figure 1). The *y*-intercept, the estimated value of C_{PSOM} MM when C_{PSOM} CM is zero, is 0.0335 with a standard error of 0.1054. The slope, the estimated change in C_{PSOM} MM per unit change in C_{PSOM} CM, is 1.1612 with a standard error of 0.0144. The estimated slope is 1.1612. The lower limit of the 95% confidence interval for the slope is 1.1320, and the upper limit is 1.1905. The estimated intercept is 0.0335. The lower limit of the 95% confidence interval for the intercept is −0.1806, and the upper limit is 0.2477.

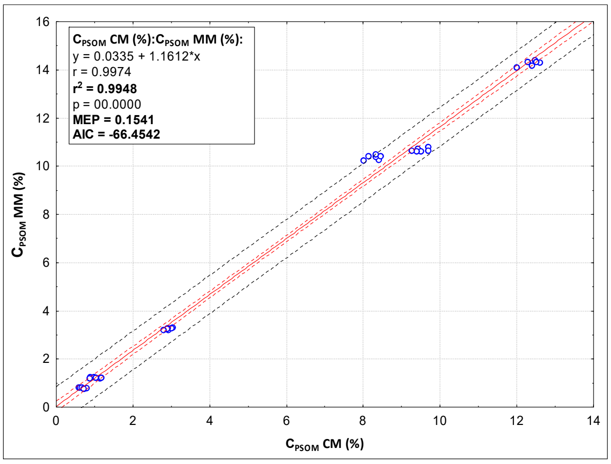


Figure 1. Linear regression dependence between the carbon of primary soil organic matter contents determined by classical and modified methods. Note: C_{PSOM} CM—the carbon belonging to primary soil organic matter determined with the classical method (%); C_{PSOM} MM—the carbon belonging to primary soil organic matter determined with the modified method (%).

Other statistically significant linear regression is the dependence between C_{HA+FA} and C_{SOF} content (data from all six localities). The equation of the straight line relating C_{SOF} and C_{HA+FA} is estimated as: $C_{SOF} = (-0.0878) + (0.6732)\ C_{HA+FA}$ using the 36 observations in this dataset. The statistical characteristics of the regression are as follows: R = 0.9894, $R^2 = 0.9789$, MEP = 0.0607, AIC = −100.0999. The model is significant according to the Fisher–Snedecor model significance test (F = 1579.8090, quantile F = 4.1300, $p = 4.3553 \times 10^{-30}$). The model shows multicollinearity (M_T) according to Scott's criterion of multicollinearity (SC = 0.3327, M_T is at the lower end of the test $M_T < 0.33$, the model is not significantly affected by multicollinearity, and, therefore, there is no need to modify the model [33]). The assumption of homoscedasticity for residuals was validated (Cook–Weisberg test). Residuals have a normal distribution (Jarque–Bera Test). Residuals are positively autocorrelated (Durbin–Watson test) (Figure 2). The *y*-intercept, the estimated value of C_{SOF} when C_{HA+FA} is zero, is −0.0878 with a standard error of 0.0609. The slope, the estimated change in C_{SOF} per unit change in C_{HA+FA}, is 0.6732 with a standard error of 0.0169. The estimated slope is 0.6732. The lower limit of the 95% confidence interval for the slope is 0.6387, and the upper limit is 0.7076. The estimated intercept is −0.0878. The lower limit of the 95% confidence interval for the intercept is −0.2116, and the upper limit is 0.0361.

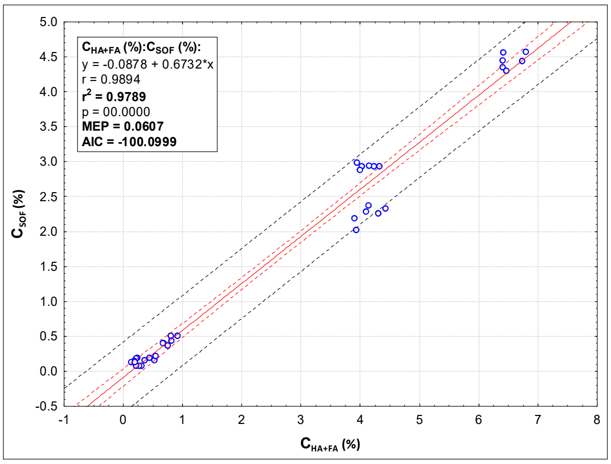


Figure 2. Linear regression dependence between the carbon belonging to humic acids and fulvic acids and the carbon belonging to stable organic fractions. Note: C_{HA+FA}–the carbon belonging to humic acids and fulvic acids (%); C_{SOF}–the carbon belonging to stable organic fractions (%).

The developed linear regression models (for C_{PSOM} and C_{SOF} parameters) show ($R^2 = 0.9948$ and 0.978, respectively) that the modified method is consistent with the classical method.

Table 2 shows the results of SOM fractionation according to Chan et al. [28]. This method makes it possible to compare the percentage carbon content which belongs to the individual fractions according to oxidation resistance. It is then possible to compare the amount of carbon in the individual fractions and compare the individual samples with each other too. Some differences between the samples can be observed, so this method is useful for comparing samples. If we had evaluated the samples only according to the amount of labile organic matter, Fraction 1 would have been the most valuable. However, this is a very simplistic and, therefore, incorrect view. Thus, the interpretation and significance of the results for evaluating the quantity and quality of SOM are questionable.

Table 2. Determination of the degree of stability of soil organic matter by oxidation resistance according to Chan's et al. method [28] in samples A, B, C, D, E, F by division into four fractions with a representation of the C content in % of the total amount of TOC (±SD).

Fraction	Sample					
	A	**B**	**C**	**D**	**E**	**F**
1	$31.42 \pm 1.16^{b}_{c}$	$34.88 \pm 1.72^{c}_{d}$	$35.92 \pm 1.87^{c}_{d}$	$18.03 \pm 0.76^{a}_{a}$	$16.97 \pm 0.96^{a}_{a}$	$30.33 \pm 2.26^{b}_{d}$
2	$25.25 \pm 0.81^{ab}_{b}$	$28.00 \pm 1.93^{b}_{c}$	$23.92 \pm 1.71^{a}_{b}$	$25.93 \pm 1.82^{ab}_{b}$	$23.92 \pm 0.82^{a}_{b}$	$26.43 \pm 1.50^{ab}_{b}$
3	$17.80 \pm 0.59^{c}_{a}$	$15.38 \pm 0.83^{b}_{a}$	$12.38 \pm 1.15^{a}_{a}$	$20.42 \pm 0.66^{d}_{a}$	$18.10 \pm 0.68^{c}_{a}$	$15.03 \pm 0.54^{b}_{a}$
4	$25.53 \pm 1.44^{b}_{b}$	$21.73 \pm 2.78^{a}_{b}$	$27.78 \pm 1.83^{b}_{c}$	$35.62 \pm 1.78^{c}_{c}$	$41.02 \pm 0.85^{d}_{c}$	$28.20 \pm 1.75^{b}_{bc}$

Note: Fraction 1 = 12N H_2SO_4 (labile); Fraction 2 = 18N–12N H_2SO_4 (semi-labile); Fraction 3 = 24N–18N H_2SO_4 (semi-stable); Fraction 4 = TOC-24N H_2SO_4 (stable); significant differences between samples within fractions are shown in upper case letters (Tukey's honest significance test; $p = 0.05$); significant differences between fractions within individual samples are shown in lower case letters (Tukey's honest significance test; $p = 0.05$).

3.2. Evaluation of Soil Organic Matter Quality

The results obtained by evaluating SOM quality according to the MM are shown in Table 3. The SOF quality expressed in CEC value showed significant differences between some samples ($F_{(5, 30)} = 608.62$; $p < 0.00001$). It is possible to distinguish four groups according to quality. The highest quality of this fraction was found in samples C and F. In addition, the evaluation of the quality of the PSOM fraction expressed by the constant k showed significant differences between the evaluated samples ($F_{(5, 30)} = 776.67$; $p < 0.00001$). It is possible to distinguish even five qualitative groups.

Table 3. Expression of stable organic fraction quality by the cation-exchange capacity of humic substances according to a Modified method (MM), by the C_{HA}:C_{FA} ratio and quotient $E_{4/6}$ according to a Classical method (CM) and expression of primar soil organic matter quality by speed constant k of its oxidation according to MM (±SD).

Parameter	Method	Sample					
		A	**B**	**C**	**D**	**E**	**F**
CEC	MM	3012 ± 86^{c}	1978 ± 93^{a}	4088 ± 119^{d}	2196 ± 31^{b}	2261 ± 43^{b}	3991 ± 99^{d}
C_{HA}:C_{FA}	CM	0.96 ± 0.16^{b}	0.75 ± 0.08^{ab}	1.71 ± 0.19^{c}	0.82 ± 0.13^{b}	0.53 ± 0.05^{a}	0.98 ± 0.17^{b}
$E_{4/6}$	CM	14.30 ± 0.57^{c}	3.55 ± 0.22^{b}	4.13 ± 0.12^{b}	2.81 ± 0.26^{a}	3.59 ± 0.19^{b}	2.67 ± 0.25^{a}
Speed constant k (s)	MM	3.16 ± 0.08^{d}	4.49 ± 0.11^{e}	0.81 ± 0.08^{a}	2.06 ± 0.12^{b}	1.88 ± 0.06^{b}	2.65 ± 0.14^{c}

Note: CEC–the cation-exchange capacity of stable organic fractions (mmol chem. equiv. H^+/1000 g); C_{HA}:C_{FA}–the ratio of carbon that belongs to humic acids and fulvic acids; $E_{4/6}$–the quotient $E_{4/6}$; significant differences between samples within parameters are shown in upper case letters (Tukey's honest significance test; $p = 0.05$).

Evaluation according to CM by the C_{HA}:C_{FA} did not prove as sensitive as the SOF quality evaluation according to their CEC. Evaluation of the quotient $E_{4/6}$ revealed completely different results. According to $E_{4/6}$, the humus quality in samples D and F was the best, while it appeared partly different according to both CM and the MM. The results of the evaluation of the quotient $E_{4/6}$ seem confusing.

A statistically significant linear regression dependence between CEC and C_{HA}:C_{FA} was demonstrated (data from all six localities). The equation of the straight line relating C_{HA}:C_{FA} and CEC is estimated as: C_{HA}:C_{FA} = (0.1266) + (0.0003) CEC using the 36 observations in this dataset. The statistical characteristics of the regression are as follows: R = 0.7001, $R^2 = 0.4901$, MEP = 0.0598, AIC = −96.9097. The model is significant according to the Fisher–Snedecor model significance test (F = 30.7672, quantile F = 4.1490, $p = 4.0459 \times 10^{-6}$). The model is correct according to Scott's criterion of multicollinearity (SC = 0.3223). The residuals passed tests for heteroskedasticity (Cook–Weisberg test). Residuals have a normal distribution (Jarque–Bera Test). Residuals are positively autocorrelated (Durbin–Watson test) (Figure 3). The y-intercept, the estimated value of C_{HA}:C_{FA} when CEC is zero, is

0.1266 with a standard error of 0.1446. The slope, the estimated change in C_{HA}:C_{FA} per unit change in CEC, is 0.0003 with a standard error of 0.0000. The estimated slope is 0.0003. The lower limit of the 95% confidence interval for the slope is 0.0002 and the upper limit is 0.0004. The estimated intercept is 0.1266. The lower limit of the 95% confidence interval for the intercept is −0.1678 and the upper limit is 0.4211.

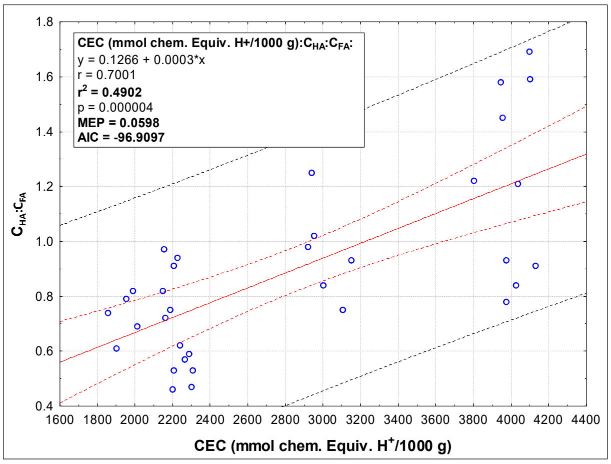


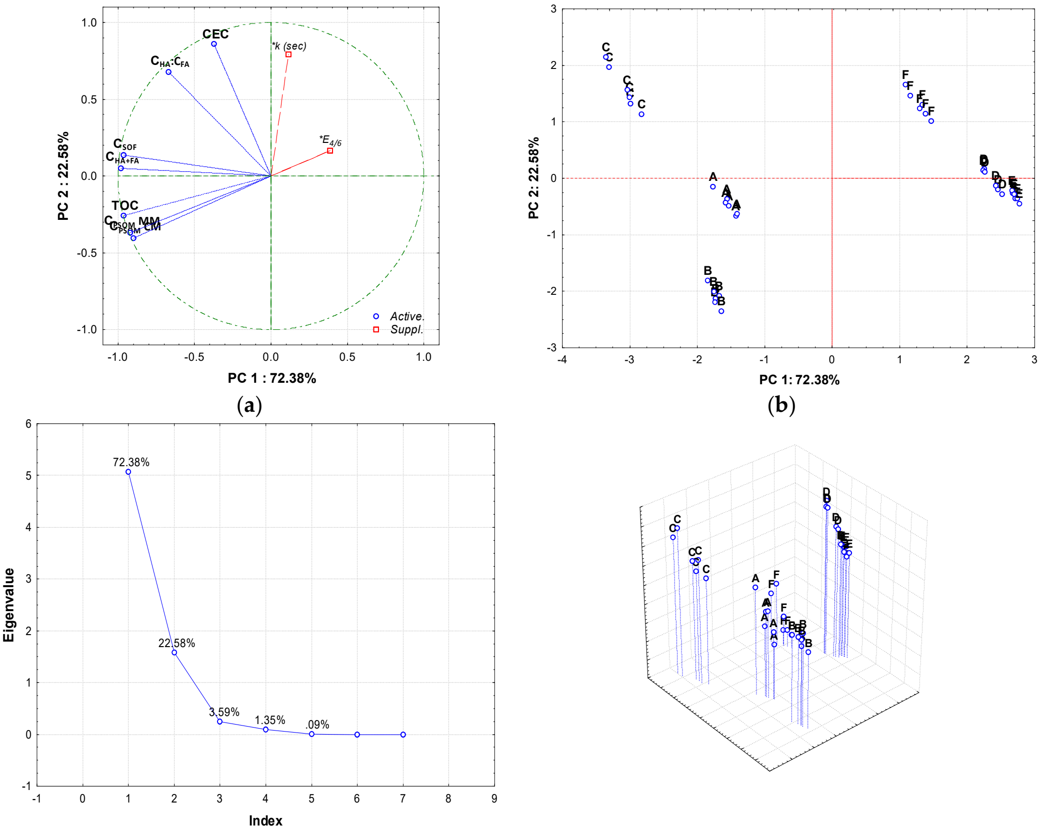
Figure 3. Linear regression of dependence between cation-exchange capacity (CEC) and the ratio of carbon that belongs to humic acids and fulvic acids (C_{HA}:C_{FA}).

3.3. Evaluation of Results from the Point of View Principal Component Analysis and Factor Analysis

On the graph of component weights PC1, PC2, and PC3 (Figure 4), the first two axes are significant, which together exhaust about 95% of the variability. The PC1 axis in the PC1 × PC2 graph unambiguously characterizes C_{HA+FA}, C_{SOF}, which go directly along this axis and are correlated with it at a level exceeding −0.96 and −0.98 (high negative correlation) as well as TOC (r = −0.96). Furthermore, on the PC1 axis, there is a very significant correlation between C_{PSOM} MM and C_{PSOM} CM (r = −0.89 and −0.91). On the PC2 axis, there is a significant correlation between CEC and $C_{HA:CFA}$ (r = 0.85 and 0.67). In the scatterplot of the component score along the PC1 axis, sampling sites according to C_{HA+FA}, C_{SOF}, TOC, and also C_{PSOM} MM and C_{PSOM} CM are clearly located. The PCA divided the sites of interest into two distinct clusters (arable land and forest land).

Factor analysis (Figure 5) confirmed the results of PCA and differentiated similarly to the PCA method of the group of localities (see scattering diagrams of component scores).

Factor weights explain the correlations between factors and features (Table 4). They represent essential information on which the interpretation of factors is based. Factor 1 describes the properties in terms of C_{PSOM} MM, C_{PSOM} CM, TOC, C_{HA+FA}, and C_{SOF}. Factor 2 clearly describes CEC and $C_{HA:}C_{FA}$. Communality represents the proportion of character variability expressed by the factors in question. It is similar to the value of R^2, which we obtain when the original characters are explained by regression by selected factors [33]. From the contribution of Factor 1 and Factor 2 to communality, it is clear how communality acquires high values (more than 0.9). Thus, the features of most values (TOC, C_{SOF}, C_{HA+FA}, C_{PSOM} CM and C_{PSOM} MM) are very well considered by the proposed factor model. For CEC and $C_{HA:}C_{FA}$ parameters, communality is at a lower level (0.5–0.7).



(a) (b)

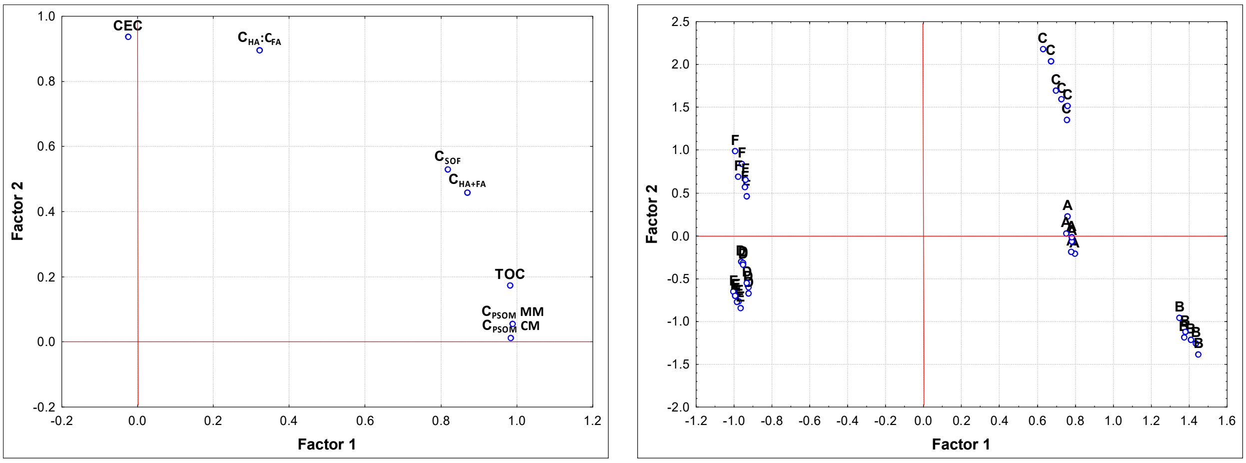
(c) (d)

Figure 4. Principal component analysis of soil organic matter parameters (TOC, C_{SOF}, C_{HA+FA}, $C_{HA:CFA}$, C_{PSOM} CM, C_{PSOM} MM, CEC, constant *k*, quotient E4/6) in various soil samples: (**a**) Graph of component weights 1 and 2 (PC1 × PC2) for soil organic matter parameters; (**b**) the scatterplot of the component score PC1 × PC2 for individual localities; (**c**) scree plot; (**d**) 3D graph PC1 × PC2 × PC3 for individual localities. Note: TOC–total organic carbon (%); C_{SOF}–the carbon belonging to stable organic fractions (%); C_{HA+FA}–the carbon belonging to humic acids and fulvic acids (%); C_{PSOM} CM–the carbon belonging to primary soil organic matter determined by the classical method (%); C_{PSOM} MM—the carbon belonging to primary soil organic matter determined by the modified method (%); CEC–the cation-exchange capacity of stable organic fractions (mmol chem. equiv. H^+/1000 g); C_{HA}:C_{FA}–the ratio of carbon that belongs to humic acids and fulvic acids; *k* (sec) –the speed constant of oxidation.

Table 4. Factor weights and contributions of a given factor to the communality for individual traits after rotation of varimax normalized soil organic matter.

Parameter	Factor Weights		Contributions of a Given Factor to the Communality		
	Factor 1	**Factor 2**	**Factor 1**	**Factor 2**	**Communalities**
TOC	0.9832	0.1733	0.9104	0.9511	0.9378
C_{SOF}	0.8182	0.5294	0.5823	0.9100	0.9055
C_{HA+FA}	0.8702	0.4587	0.6724	0.9258	0.9220
C_{PSOM} CM	0.9849	0.0110	0.9266	0.9276	0.9213
C_{PSOM} MM	0.9893	0.0545	0.9328	0.9387	0.9286
CEC	−0.0249	0.9355	0.0000	0.5730	0.5360
C_{HA}:C_{FA}	0.3227	0.8953	0.0775	0.8036	0.7428

Note: TOC–total organic carbon (%); C_{SOF}–the carbon belonging to stable organic fractions (%); C_{HA+FA}–the carbon belonging to humic acids and fulvic acids (%); C_{PSOM} CM–the carbon belonging to primary soil organic matter determined by the classical method (%); C_{PSOM} MM–the carbon belonging to primary soil organic matter determined by the modified method (%); CEC–the cation-exchange capacity of stable organic fractions (mmol chem. equiv. H^+/1000 g); C_{HA}:C_{FA}–the ratio of carbon that belongs to humic acids and fulvic acids.



(**a**) (**b**)

Figure 5. Factor analysis of soil organic matter parameters (TOC, C_{SOF}, C_{HA+FA}, $C_{HA:CFA}$, C_{PSOM} CM, C_{PSOM} MM, CEC) in individual localities: (**a**) graph of factor weights (Factor 1 × Factor 2) for soil organic matter parameters; (**b**) scattering diagram of component scores Factor 1 × Factor 2 for individual localities. Note: TOC–total organic carbon (%); C_{SOF}–the carbon belonging to stable organic fractions (%); C_{HA+FA}–the carbon belonging to humic acids and fulvic acids (%); C_{PSOM} CM–the carbon belonging to primary soil organic matter determined by the classical method (%); C_{PSOM} MM–the carbon belonging to primary soil organic matter determined by the modified method (%); CEC–the cation-exchange capacity of stable organic fractions (mmol chem. equiv. H^+/1000 g); C_{HA}:C_{FA}–the ratio of carbon that belongs to humic acids and fulvic acids.

4. Discussion

The CM is based on the isolation of humic substances by alkaline extraction of the soil sample and the precipitation of humic acids from the extract in an acidic environment. Therefore, they have some weaknesses. These include the impossibility of capturing all the extracted carbon or the blurred boundary between humidified and non-humidified organic material [34–37]. The Humification model on which the procedures in CM are based is therefore sometimes questioned [34,38]. Classical humification has been supplemented with selective preservation [39] and a progressive decomposition model (so-called "degradation concept") [36]. Lehmann and Kleber [34] consider SOM as a continuum of progressively decomposing organic compounds and question the high resistance of humic acids to decomposition. The "Soil continuum model" focuses on the ability of decomposer organisms to access SOM and on the protection of organic matter from decomposition provided by soil minerals. Except for mineralization and humification, the stabilization of SOM must also be respected [40]. For these reasons, the procedures used in CM as comparative should only be considered roughly indicative.

The MM is not based on the alkaline extraction of organic matter from the soil sample. However, results may also be affected by specific problems. Chemical oxidation is only the simulation of the biodegradation process in natural conditions. Another disadvantage is that, for example, lignins belong to a stable fraction of SOM according to this method. However, they can be transformed by microorganisms in the soil [41]. Thus, the division into labile and stable organic fractions in the soil is not flawless. Only black carbon fraction, in particular, is difficult to decompose. Therefore, it is generally considered to be a stable fraction [42,43]. Another organic matter is more or less degradable. Thus, in MM, the boundary between labile and stable organic fractions was clearly defined. The part of SOM which resists oxidation in defined conditions (0.4 mol/L solution of $K_2Cr_2O_7$ in 12 M of H_2SO_4 at 90 °C for 30 min) is considered stable.

During the PSOM quality assessment, we encountered specific procedural obstacles. It was problematic to maintain a constant temperature of 100 °C, which Maroušek et al. [31] use in their method. Therefore, we tried to optimize the method. Repeated empirical experiments have led us to conclude that a constant temperature is the best maintained in a water bath (compared to a laboratory thermostat or thermoblock). However, due to the boiling point of the water, we decreased the temperature to 90 °C. We also changed the time intervals during which SOM is oxidized. We used 40 min for the fourth flask (instead of 45 min). Thus, all intervals of oxidation are the same in terms of time. These measures can logically lead to less organic carbon being determined in the C_{PSOM} fraction than at the original conditions (higher temperature and longer oxidation time).

Considering the quality of PSOM, it is the most stable in sample C. In terms of plant nutrition, this is not a positive phenomenon. This component of SOM should be a source of energy for soil edaphon and reserve plant nutrients. Thus, the higher lability of PSOM is particularly appreciated [20,22,44]. On the other hand, it should be considered that, at the appropriate temperature and humidity conditions, microbial biomass can rapidly multiply, resulting in rapid mineralization of organic matter and the most labile fractions being consumed rapidly [45]. The amount of non-humified soil fraction is always proportional to microbial biomass in the soil [46].

The MM reports that the C_{SOF} content is substantially lower than CM for all samples (CM expressed the amount of carbon attributable to humic substances C_{HA}+C_{FA}). This is because CM captures fulvic acids in addition to humic acids in this fraction. In contrast, in the MM, the more labile fulvic acids are oxidized, and their carbon then enriches the C_{PSOM} fraction. The stability of humic acids cannot be doubted. Humic acids are incomparably more resistant to decomposition than fulvic acids [47]. Thus, labile fulvic acids do not belong to the stable soil organic fraction with certainty.

According to the statistical evaluation, the determination of the CEC of the SOF fraction cannot be considered an equivalent substitute for the C_{HA}:C_{FA}. Nevertheless, CEC is a good indicator of soil quality [48,49]. This fact was more less confirmed in this research. Moral and Rebollo [50] deem the CEC a sensitive indicator for determining the soil's nutrient holding capacity, fertility, and long-term productivity. This parameter can be an additional characteristic to evaluate SOM quality in various ecosystems (fields, forests, etc.). Moreover, the determination of the CEC of the SOF fraction is much less laborious and less time-consuming than determining the C_{HA}:C_{FA}.

The proposed MM is not intended for deep scientific investigation. It should give information to practical farmers about the condition of SOM. Information about SOM conditions will help farmers decide whether to apply more or less rapidly mineralizing fertilizers (such as slurry or green manure) or fertilizers with more stabilized organic matter, such as manure, compost or even digestate from biogas station. Thus, the farmers who have detailed information on SOM quality can make the right decisions about applying various agrotechnical measures to increase the microbial activity of the soil, which is crucial for improving soil fertility.

PSOM quality evaluation by determining the speed constant k of organic matter oxidation can also be used for other organic materials, such as biochar, organic waste, and compost. The classical method does not allow these data to be determined.

5. Conclusions

Six soil samples were analyzed by a Modified method, which is cheap and instrumentally undemanding. The samples were also analyzed in parallel by the currently used procedures based on the already obsolete humification model. The results were compared with each other. It was found that very similar results were achieved in the evaluation of SOM content. The performed principal component analysis and factor analysis confirm the results of linear regression models for parameters (C_{PSOM} and C_{SOF}). It was found that the newly used working procedures are consistent with the original methods of fractionation of humic substances. The analysis of samples thus confirmed that obsolete lengthy methods of assessing the quantity of SOM could be replaced by the Modified method. Multi-dimensional statistical methods have shown that the newly determined parameter, the CEC of the stable organic fraction, cannot fully replace the classic C_{HA}:C_{FA} parameter due to low communality. Therefore, we can only use it as an additional parameter to evaluate SOM quality. However, compared with classical procedures, the modified method enables assessing the quality of PSOM through the speed constant k of its oxidation. This part of SOM is essential for soil microorganisms, and it serves as a source of plant nutrients. Thus, information about its quality is very valuable. The obtained results give clear information on the state of SOM. By ingeniously applying suitable organic fertilizers, the farmers can improve soil properties, including soil fertility. It is planned to continue similar research, assessing more soil species and types to deepen the knowledge of the benefits of the new method.

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Publikace 2: Vliv vybraných pěstebních technologií kukuřice na změny labilní frakce půdní organické hmoty v písčito-hlinité kambizemi

Kopecký, M., Peterka, J., Kolář, L., Konvalina, P., Maroušek, J., Váchalová, R., ... & Tran, D. K. (2021). Influence of selected maize cultivation technologies on changes in the labile fraction of soil organic matter sandy-loam cambisol soil structure. *Soil and Tillage Research, 207,* 104865. DOI: 10.1016/j.still.2020.104865.

Intenzita rozkladu a syntézy organických látek v půdě závisí na charakteru samotné organické hmoty, pH, výživném režimu a zrnitostním složení půd, hydrotermických podmínkách stanoviště a dalších podmínkách prostředí (Angst et al., 2021; Sierra et al., 2015). Také ale na biologické aktivitě půdy. Charakter využití uhlíku obecně závisí na typu mikroorganismů (tj. houby a aktinomycety vs. bakterie, oligotrofy vs. kopiotrofy atd.) (Chenu et al., 2019). Mikroorganismy přispívají jak k biodegradaci a mineralizaci půdních organických substrátů, tak ke vzniku nových organických metabolitů. Jejich působení tedy vede ke snížení ukládání uhlíku (prostřednictvím mineralizace POH), ale zároveň zvýšení doby jeho zdržení, protože jejich metabolity vykazují vysokou afinitu k ochranným minerálním fázím (Cotrufo et al., 2013; Kallenbach et al., 2015; Miltner et al., 2012). Rychlost přeměn je omezena fyzickou dostupností substrátu pro mikroorganismy nebo jejich enzymy (např. Juarez et al., 2013; Pinheiro et al., 2015; Ruamps et al., 2011). Z důvodů různé ochrany POH před rozkladem nemusí nutně přirozeně „odolná“ biomolekula v půdě přetrvávat, a naopak „labilní“ biomolekuly se nemusí nutně rozkládat (Angst et al., 2021). Lange et al. (2015) se domnívají, že zvýšení ukládání uhlíku je omezeno především integrací nového uhlíku do půdy a méně pak rozkladem půdního uhlíku stávajícího.

Specifický vliv na POH mají též žížaly. Při zkoumání jejich působení byly pozorovány velmi kontrastní výsledky (Lubbers et al., 2013). Vysvětlení je takové, že žížaly mají dva opačné účinky na zásoby POH v různých časových měřítcích. Současně zvyšují mineralizaci čerstvé i staré POH (fragmentací, vlastním dýcháním a stimulací půdních mikroorganismů) a začleňují čerstvé zbytky do agregátů a pohřbívají uhlík do hloubky, což zvyšuje jejich stabilizaci (Schon et al., 2015).

Významný vliv na obsah kyslíku a tím i na mikrobiální aktivitu má kultivace půdy (Johnston et al., 2009). Změny v praxi polního managementu mohou změnit chemické vlastnosti POH (Moraes et al., 2011). Obecně se má za to, že zpracování půdy zvyšuje mineralizaci POH v důsledku mechanického a deštěm vyvolaného rozrušování půdních agregátů a následného uvolňování CO_2. Spaccini et al. (2006) uvádí progresivní pokles koncentrací huminových látek v půdách, které byly převedeny z lesního hospodářství na ornou půdu. Pokles připisují mikrobiální oxidaci organických materiálů dříve chráněných v půdních agregátech zničených kultivací. Proto je považováno za vhodný postup pro zvýšení/udržení zásob POH bezorebné zpracování půdy. Výsledky globálních metaanalýz a přehledů potvrzují, že zásoby organického uhlíku v půdě se zvyšují v horních vrstvách (0–15 nebo 0–20 cm) v bezorebném zpracování. Ukazují ale nízký až nevýznamný účinek v hloubce větší než 30 cm. Zdá se, že je tomu tak zejména ve vlhkých a mírných podmínkách (např. Dimassi et al., 2014; VandenBygaart et al., 2010).

Jak vyplývá z výše uvedeného textu, přeměny POH v půdě jsou ovlivněny komplexem nejrůznějších faktorů. Namísto hodnocení změn prostřednictvím celkového obsahu POH, je vhodné sledovat změny v různých frakcích (Guimarães et al., 2013). Citlivými indikátory změn kvality půdy jsou frakce labilní (Bayer et al., 2002; Haynes, 2005). Nejlabilnější frakce POH je v půdě zastoupena jen ve velmi malém množství, přesto přímo ovlivňuje půdní mikroorganismy, kterým slouží jako živinný substrát (Schmidt et al., 2011), a zprostředkovaně i půdní úrodnost.

V článku byly hledány citlivé ukazatele transformací labilních frakcí POH, které by změny ukázaly i v krátkodobém experimentu. Výzkum probíhal na modelové plodině kukuřici seté, která je označována jako erozně nebezpečná plodina. Protože vodní eroze ohrožuje téměř polovinu zemědělské půdy v ČR, byly v experimentu využity různé technologie zakládání porostů, které jsou z hlediska vodní eroze k životnímu prostředí šetrnější. Jedná se o technologie strip-till a no-till. Jako třetí technologie byla zvolena příprava půdy diskováním, které je v evropských podmínkách relativně běžné.

Experiment byl proveden ve středních Čechách na polích s hlinitopísčitou kambizemí. Cílem tohoto výzkumu bylo posoudit zmíněné technologie z hlediska labilních frakcí půdní organické hmoty a strukturního stavu půdy. Hodnocení organické hmoty v tomto případě nebylo založeno na sledování její odolnosti vůči oxidaci, ale podle specifických stabilizačních mechanismů. Selektivní ochranou proti biodegradaci POH je prostorová nedostupnost a interakce s minerálními povrchy (von Lützow et al., 2006). Existují dva hlavní mechanismy fyzikální stabilizace, a to fyzická ochrana v půdních agregátech (Six et al., 2004) a stabilizace organické hmoty tvorbou organo-minerálních komplexů (Llorente et al., 2010).

Agregátový rozbor se jako citlivý indikátor neuplatnil (byl zaznamenán jen rozdíl v množství makroagregátů mezi technologiemi diskování a strip-till). Ještě méně citlivými ukazateli byly celkový uhlík a celkový dusík v půdě. Tato práce naopak potvrdila zjištění, že velmi citlivým indikátorem změn POH vyvolaných různými typy hospodaření s půdou je obsah dusíku v partikulární organické hmotě, která je definována velikostí 53–2000 µm (Yu et al., 2022). Nejvyšší obsah dusíku v partikulární organické hmotě byl zaznamenán u varianty no-till. Nemusí to ale nutně znamenat jeho vyšší přístupnost pro rostliny (Sharifi et al., 2008). V této technologii byl zjištěn i nejvyšší obsah organického uhlíku v mikro i makroagregátech. Je tedy jasné, že v této variantě je organická hmota nejlépe chráněna před rozkladem. Na druhé straně vysoký obsah labilních frakcí POH podporuje biologickou aktivitu půdy, a tím i vysokou potenciální úrodnost půdy. Z tohoto pohledu byla nejlepší variantou managementu metoda strip-till, u níž byl zjištěn nejvyšší obsah uhlíku v partikulární organické hmotě i nejvyšší obsah vodou extrahovatelného uhlíku, což je důležité z agronomického hlediska. Spolehlivým indikátorem byl také vodou extrahovatelný dusík.

Abstract

Disc cultivators are a commonly used method in soil processing when growing maize in Central Europe. However, the slope of the land leads to soil losses through water erosion. Therefore, conservation technologies for soil treatment—strip-till and no-till—are recommended. The aim of this research was to assess these technologies in terms of the labile fractions of soil organic matter and the structural state of the soil. Another goal of the work was to find the most sensitive indicators of change in the labile fractions of soil organic matter, which would indicate changes even over a relatively short-term experiment (three years). The experiment was conducted in Central Bohemia, Czech Republic on plots of sandy-loam cambisol. Changes in soil structure and carbon and nitrogen content in various soil fractions were monitored. The obtained results of two soil conservation technologies (strip-till, no-till) were compared with the results for a commonly used technology (disc cultivation). The strip-till technology led to the highest accumulation of a very labile fraction of organic soil matter and the most sensitive indicator of change was the content of water-extractable organic carbon. The no-till technology protected the soil organic matter from decomposition by physical protection in soil aggregates. Most of the soil organic matter remained un-decomposed. Sensitive indicators of change were the nitrogen content in particulate organic soil matter and the content of water-extractable organic nitrogen. It was found that changes in the labile fraction of soil organic matter can be monitored through suitable indicators during a short-term experiment. Furthermore, we found that no-till technology contributes to the protection of unstable soil organic matter against decomposition, especially through physical protection in soil aggregates. In terms of the content of labile fractions of soil organic matter and their possible effect on the potential soil fertility, it was shown in this short-term experiment that strip-till technology was optimal.

Keywords: Indicators Labile fractions Soil organic matter Soil structure

Publikace 3: Black carbon a jeho vliv na sekvestraci uhlíku v půdě

Kopecký, M., Kolář, L., Váchalová, R., Konvalina, P., Batt, J., Mráz, P., ... & Dumbrovský, M. (2021). Black Carbon and Its Effect on Carbon Sequestration in Soil. *Agronomy*, *11*(11), 2261. DOI: 10.3390/agronomy11112261.

Množství POH na jakémkoli místě se v průběhu času mění v závislosti na přidaném fotosyntetickém uhlíku a na rychlosti jeho rozkladu (Wander a Nissen, 2004). Tato publikace je, na rozdíl od předešlé, věnována frakci black carbon, která je obecně považována za stabilní. Její rozklad by tedy měl být pomalý a uhlík v ní obsažený by měl být v půdě uložen dlouhodobě (Schmidt a Noack, 2000; Schmidt et al., 2002). Frakci black carbon se začal věnovat Goldberg (1985). Uvádí, že pochází převážně z nedokonalého spalování fosilních paliv, dřeva a biomasy a také z určitých průmyslových procesů, je porézní a obsahuje zhruba 85–98 % uhlíku. Dle Masiello (2004) se black carbon skládá ze složitých polyaromatických kondenzovaných struktur. Schmidt a Noack (2000) uvádí, že black carbon představuje kontinuum od částečně zuhelnatělého materiálu po částice grafitu a sazí, ovšem bez obecné shody o jasných hranicích. S problematickou charakterizací black carbonu se ztotožňují i Hammes et al. (2006). De la Rosa et al. (2008) se domnívají, že tato žáruvzdorná organická hmota je v životním prostředí všudypřítomná.

Cílem příspěvku bylo ověřit, zda se black carbon nachází v geografické oblasti jižních Čech a jaký má vliv na ukládání uhlíku do půdy. Bylo pracováno s hypotézou, že se v půdě budou vyskytovat dva „druhy“ black carbonu. Prvním z nich je velmi starý historický black carbon (HBC), který pochází z dávných požárů biomasy. Druhým je pak black carbon antropogenní (ABC). Ten vzniká jako produkt nedokonalého spalování (doprava, lokální topeniště apod.) a je mnohem mladší. Na základě předpokladu míry znečištění půdy způsobeného člověkem bylo vytipováno 20 vzorkovacích míst. Polovina z nich byla v lokalitách bez zvýšené depozice spadu, druhá polovina v blízkosti větších lidských sídel.

V průměru byl zjištěn nižší obsah black carbonu v řídce osídlených oblastech jižních Čech (2,16 % C_{org}). V oblastech větších měst s výraznou antropogenní zátěží byl jeho obsah vyšší (2,76 % C_{org}). Black carbon v půdách u větších měst tedy má pravděpodobně antropogenní původ. Dále bylo zjištěno, že dávno uložený HBC je silně vázán nejen na méně stabilní volnou lehkou frakci, ale také na těžkou minerální koloidní frakci půdy. Naopak ABC se dosud s minerálními koloidy stabilně nespojil. Může to být proto, že je méně stabilní než HBC, nebo z důvodu, že zatím v půdě nestačil oxidovat. Na jeho povrchu se tedy nevytvořila záporně nabitá místa karboxylových a jiných funkčních skupin. Antropogenní black carbon má tedy pouze schopnost sorpční, nikoli iontovýměnnou. Pro pevné spojení minerální koloidní jílové frakce s koloidní organickou frakcí je iontovýměnná schopnost významnější než schopnost sorpční (Cheng et al., 2006).

Protože těžká půdní frakce není ovlivněna ABC, je pravděpodobné, že bude v půdě snadněji podléhat rozkladu (Seiler a Crutzen, 1980). Obecné představy o mimořádné odolnosti black carbonu vůči rozkladu je proto nutné brát s jistou rezervou (Kuhlbusch et al., 1996; Schmidt a Noack, 2000). To vyplývá i ze zjištění, že vysoká sorpční kapacita ABC vedla k tvorbě okludované lehké frakce POH, což je stabilizačním mechanismem (Lugato et al., 2009). Přesto platí, že i tato organická hmota mineralizuje v půdě v řádu desetiletí (Llorente et al., 2010). Trvalým uložištěm uhlíku tedy ABC není.

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Black Carbon and Its Effect on Carbon Sequestration in Soil

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Abstract: The properties of black carbon (BC) are described very differently in the literature, even when determined by the same methodological procedure. To clarify this discrepancy, BC was investigated in the clay Cambisols of southern Bohemia, Czech Republic, in groups of soils with lower and higher deposition of its atmospheric fallout. The BC determination was performed according to a modified method of Kuhlbusch and Crutzen (1995). The amount of the free light fraction, the occluded light fraction of soil organic matter and its ratio, the amount of heavy soil fraction DF, and its soil organic matter DFOM were determined. Other soil characteristics were identified. It was found that there are two very different types of BC in soils. Historical BC from biomass fires, and new, anthropogenic, from the furnace and transport fumes. Historical BC has a significant effect on the organic matter of the heavy soil fraction, on the ratio of the free and occluded soil organic matter fraction, and the number of water-resistant soil aggregates. Anthropogenic BC does not have this effect. Because this form of BC is not significantly stabilized by the colloidal mineral fraction, it is necessary to take general data on BC's high stability and resistance to mineralization in the soil with circumspection.

Keywords: anthropogenic black carbon; density fractionation; historical black carbon; waterproof macro-aggregates

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1. Introduction

Over the last 150 years, there has been a decrease in organic carbon (C_{org}) in the world's soils [1] and a consequent increase in atmospheric CO_2 [2]. Therefore, carbon sequestration in stable and resistant fractions of soil organic matter (SOM) in the soil is very current. The concept of carbon sequestration focuses on increasing primary production (CO_2 consumption) or reducing the rate of CO_2 production by SOM mineralization [3]. Long-term carbon sequestration in soil represents stable black carbon (BC) fractions [4]. Soil organic matter consists of functional pools that differ in their rate of decomposition. The labile part is the primary source of energy for soil microorganisms and contributes to the nutrient regime of soils [5]. This applies in particular to the water-soluble part of SOM. However, other pools are also important—semilabile, stable, and inert [6]. In the past, humic substances, humic acids, humins, and partially fulvic acids were considered stable forms of soil carbon. At present, this humification model is widely criticized, and the presumed stability of humic substances is questioned [7,8]. However, criticism of this conception has also emerged [9].

In any case, in the laboratory determination, the content of humic substances in the soil is "increased" during the determination by those black carbon fractions, which, similar to humic substances, can be extracted with an alkaline solution [10,11]. Therefore, the humification model is replaced by the SOM fractionation, according to specific stabilization mechanisms. The protection of SOM against biodegradation is ensured by its spatial inaccessibility (in soil aggregates) and organic matter stabilization in the formed organomineral complexes [12–14]. Modern instrumental analysis methods (thermal analysis, nuclear magnetic resonance, and pyrolysis) have shown significant heterogeneity of humates in different soils and fractions of a single soil. Criticism of the humification model is therefore justified.

The structural features and chemical composition of highly aromatic soil humic acids (HA) suggest that these HA are derived from BC and not natural native plant materials. Humic acids from laboratory oxidized BC also show remarkable similarities in chemical compositions and spectroscopic data with highly aromatic soil humic acids. Therefore, BC is considered a possible source of the chemically most stable, aromatic soil carbon pool [15].

Black carbon is defined by Goldberg [16] as a mixed product that results from the incomplete combustion of fossil fuels, wood, and biomass, as well as from certain industrial processes, such as the production of carbon black for automobile tires and printing inks. He understood BC as a mixture of different charcoals, which he defines as a porous, solid product, containing 85–98% C, produced by carbonization of carbonaceous materials, at temperatures up to 600 °C in the absence of air. An overview of the chemical and physical properties of these substances is described by Mantell [17]. From the point of view of environmental relations, two characteristics of BC are important: high chemical stability at usual water, air, and soil temperatures, and high sorption activity, which depend on the original carbonaceous material, chemical characteristics of the environment, in which BC was formed and the reaction time and temperature during its arising [18]. Medalia and Rivin [19] distinguish four types of BC, according to particle size, their morphology, origin, and surface properties. Kuhlbusch and Crutzen [20] define BC as the fire produced carbon fraction with a molar H/C ratio of $\leq$0.2, which is resistant to heating to 340 °C in pure oxygen. The term BC includes several other terms: char, charcoal, soot, elemental carbon, pyrogenic carbon [21]. BC is considered an important sink in the global carbon pool [22]; it may represent an inert carbon pool used in SOM models [23].

It is estimated that the annual BC production from biomass combustion is 1 Tg [22], with total carbon content in the biosphere, atmosphere, and sea pools of 3×10^6 Tg. Thus, it is clear that BC destruction occurs, although it is generally considered extremely stable. Kuhlbusch et al. [24] give an estimate at 50–270 Tg per year, with more than 90% of BC coming from terrestrial ecosystems. There are a number of other estimates of BC production in the literature, but these are mostly geographically smaller units.

There are two destructive mechanisms of BC: photochemical and microbial decay. Human society releases other BC into the environment through the deliberate burning of forests and fossil fuels [4], the operation of engines vehicles, and the production of soot, graphite, and activated carbon. Recently, pyrolytic processes in the chemical industry have developed rapidly. Their solid waste, biochar, is another source of BC [25].

Most of this BC is stored in soils [26] and can form significant fractions of soil carbon [4,27]. The danger is the absorption of polycyclic aromatic hydrocarbons (PAHs) and other organic pollutants, sorb on BC [28]. Abiotic and microbial oxidation can form functional groups with a network of negative charges on the surface of BC particles [29]. A high concentration of COOH groups has been demonstrated after oxidative degradation of burned plants by dilute HNO_3 [30]. Influencing nutritional dynamics in soil has also been demonstrated [31,32]. The formation of carboxyl groups or other negatively charged groups in BC-added soils can be caused by two processes: (1) surface oxidation of BC particles themselves or (2) absorption of highly oxidized organic matter on the surface of BC particles [33]. The effect of BC oxidation on the increase in cation exchange capacity (CEC) has been demonstrated [34].

Analytical methods for the quantitative determination of BC in soils and other matrices are quite problematic due to the analyzed material's high heterogeneity and insolubility. An overview of basic methods is given by Goldberg [16]. Methods of spectroscopic, chemical oxidation [35], oxidation to CO_2 after removal of other C-components [20], the combination of spectroscopy, and nuclear magnetic resonance [36] are used. It was found that in the oxidative degradation of coal, polycyclic and substituted aromatic centers are converted to benzenecarboxylic acids—BPCA [37]. This fact also applies to coal pyrolytic residues [38]. Schnitzer [39] found that BPCAs derived only from benzene rings unsubstituted by oxygen, but only C atoms. This is a feature typical of black carbon. That is why Glaser et al. [21] assumed that BPCA could be used as a specific measure of black carbon in soils.

Hedges et al. [40] published "The carbon combustion continuum of black carbon". It shows the carbon combustion products from large, reactive particles of weakly charred biomass through char, charcoal, soot, and graphite to submicroscopic black carbon particles, and outlines possible analytical determination methods. Chemical methods are only suitable for graphite, soot and charcoal; thermochemical methods only for graphite and soot [41]; visual methods only for weakly carbonized biomass [26]. The whole area of all charred biomass products can be captured only by CP/MAS 13C NMR. The most significant part of BC components (char, charcoal) can be captured by BPCA methods [21], molecular markers [42], and ultra-high mass spectrometry [26]. Combinations of these methods are also used [20].

Black carbon can affect the long-term storage of carbon in the soil in two ways—by its own stability and by its influence on two main mechanisms of physical stabilization of organic matter in the soil, which is physical protection in soil aggregates and stabilization by the formation of organomineral complexes [12]. Macro-aggregates (>250 μm) have a higher concentration of SOM than micro-aggregates [43] because macro-aggregates contain more binders [44]. Decomposed organic material is also a transitional sealant [45]. However, tillage management also has importance here [46].

Ultrasonic dispersion of stable aggregates and determination of density allows separation into three different fractions according to various physical protection mechanisms [47]. The free SOM fraction (FF) is isolated before ultrasonic dispersion, the occluded SOM fraction (OF) is after ultrasonic dispersion. The last fraction is organomineral, so-called "heavy" (DF). Its organic matter is called DFOM. The FF fraction is labile, the OF fraction more stable. The DF fraction is very stable, with a mineralization period of decades to centuries [12,48,49]. However, even the labile FF fraction can be further divided by density fractionation. It is divided into a free light fraction of organic matter (fLFOM), which is very labile, and a more stable occluded light fraction (oLFOM). The fLFOM fraction is on the surface of the aggregates; the oLFOM fraction is inside the aggregates [50]. For oLFOM to mineralize, it must first be released from the aggregates. Therefore, oLFOM is more stable the more considerable the number of water-resistant aggregates is in the soil [51].

However, BC particles are also part of the light organic matter fraction (LFOM). Therefore, the data on the ratio of fLFOM to oLFOM are essential in studying the stability of BC in soil [52].

The work aimed to determine the relationship between the amount and properties of black carbon in the clay Cambisols of South Bohemia, Czech Republic, to the amount of water-resistant macro-aggregates, the ratio of the free occluded light fraction of organic matter and the amount of heavy fraction of organic matter. According to the results, to contribute to the discussion of whether carbon sequestration in the form of BC is more or less significant in the given soil and climatic conditions at medium altitude and in a relatively clean landscape.

2. Materials and Methods

2.1. Soil Samples Processing

Cambisols are the predominant soil type in South Bohemia. The research focused on medium-heavy soils—loam soils. Ten localities were selected where the deposition of emissions from local heating plants and motor transport can be assumed. These localities were located east of relatively large human settlements; the exact places were selected based on maps of the prevailing wind direction. Namely: Tábor, Písek, Strakonice, Prachatice, 3 × České Budějovice, 2 × Český Krumlov, Jindřichův Hradec. Another ten samples were taken from localities relatively remote from sources of anthropogenic pollution; namely Křišťanov, Záhvozdí, Slavkov, Malšín, Jaroměř, Malonty, Pohorská Ves, Paseky, Hartunkov, Rychnov. The map of sampling localities is shown in Figure S1. Sampling was performed using a pedological sampling rod on arable land from a depth of 0–0.180 mm. Twenty samples were taken from each locality (from one particular land block) and composited. Soil samples were collected in May 2020. All analyses described below were performed six times.

The method described by Kuhlbusch and Crutzen [20] was used to determine BC. This method was originally intended to determine BC in the combustion residues of various vegetation types. The organic content is too low for soil analyses. This disadvantage was minimized by removing specifically heavier mineral particles using the pipetting method commonly used to determine soil granularity. Soil samples (sieved soil < 2000 µm) were first dispersed by boiling for 30 min with alkaline solution (dissolved 35.7 g of $(NaPO_3)_6$ and 7.94 g of Na_2CO_3 per liter of water). Particles larger than 250 µm were then removed through a sieve. The resulting suspension was diluted to a uniform volume (1000 mL) and, after mixing, transferred to a sedimentation device to determine soil granularity. The procedure was the same as used for determining soil granularity by the pipetting method. A fraction smaller than 50 µm was collected. Although this method of concentration increase of organic matter in the sample results in the loss of particulate organic matter of the soil, which is usually trapped on the sieve together with the sand, the transformed primary organic matter to which BC belongs remains in the most subtle soil fraction. A further increase in the concentration of the organic component was achieved by density fractionation with a NaI solution with a density of 1.6 g/cm^3. The isolated soil particles $\leq$50 µm in the centrifuge tube were shaken in an orbital shaker (170 rpm/min) with ten 5 mm diameter glass beads with 40 mL of 1.6 g/cm^3 sodium iodide solution for 18 h. After vacuum filtration of the supernatant, the free light fraction (fLF) and the occluded light fraction (oLF) and their soil organic matter fLFOM and oLFOM were obtained. These two fractions, according to Balesdent et al. [52], contain BC. The sediment in NaI solution is a heavy fraction (DF) with a density greater than 1.6 g/cm^3.

2.2. Black Carbon Content Determination

Elemental analyses (Vario EL CUBE) of dried and pulverized fLFOM and oLFOM samples made it possible to obtain data on the samples' total carbon (TC) and total hydrogen (TH). The aliquot proportion of the samples was sequentially extracted in a centrifuge tube with 1 M NaOH, 70% HNO_3, 1% HCl and twice with deionized water. After drying and weighing the residues, a second elemental analysis was performed to determine the total carbon (TC1) and hydrogen (TH1) content after extraction. It is then possible to calculate the removed carbon and hydrogen (inorganic carbon of carbonates IC, organic carbon released by solvent extraction OC1, and hydrogen removed by solvent extraction OH2).

A second purification step is needed to remove the residual organic carbon and hydrogen (OC2, OH2)—a thermal process. Parallel weighed samples of the pretreated material were exposed to a temperature of 340 °C for 2 h in a stream of oxygen (500 mL/min). The third elemental analysis will make it possible to determine black carbon and hydrogen bound to BC (BH) after deducting the volatilized carbon by the fire (VC). The molar H/C ratio (BH/BC) determined without correction for hydrogen, possibly bound to minerals (from OC2 and OH2), which was recommended by the cited authors [20].

2.3. Determination of the Structure of Soil

Determination of the structural condition of soil samples was performed by sieving and sedimentation [53]. Water-stable aggregates were fractionated into micro-aggregates (<250 µm) and macro-aggregates (>250 µm) according to John et al. [48]: 50 g of sieved soil ($\leq$10 mm) was dried at 40 °C for 48 h and sieved in deionized water in a sieving machine for 10 min. After 50 vertical lifts of the sieve (38 mm), the water-stable aggregates

(>250 µm) were sprayed onto a vacuum filter, the water was aspirated and the aggregates dried at 40 °C. Particles that passed through the sieve (<250 µm) were isolated by the addition of 2.5 mL of 0.5 M $AlCl_3$ solution per 1000 mL of supernatant, after which they were decanted and dried for 48 h at 40 °C.

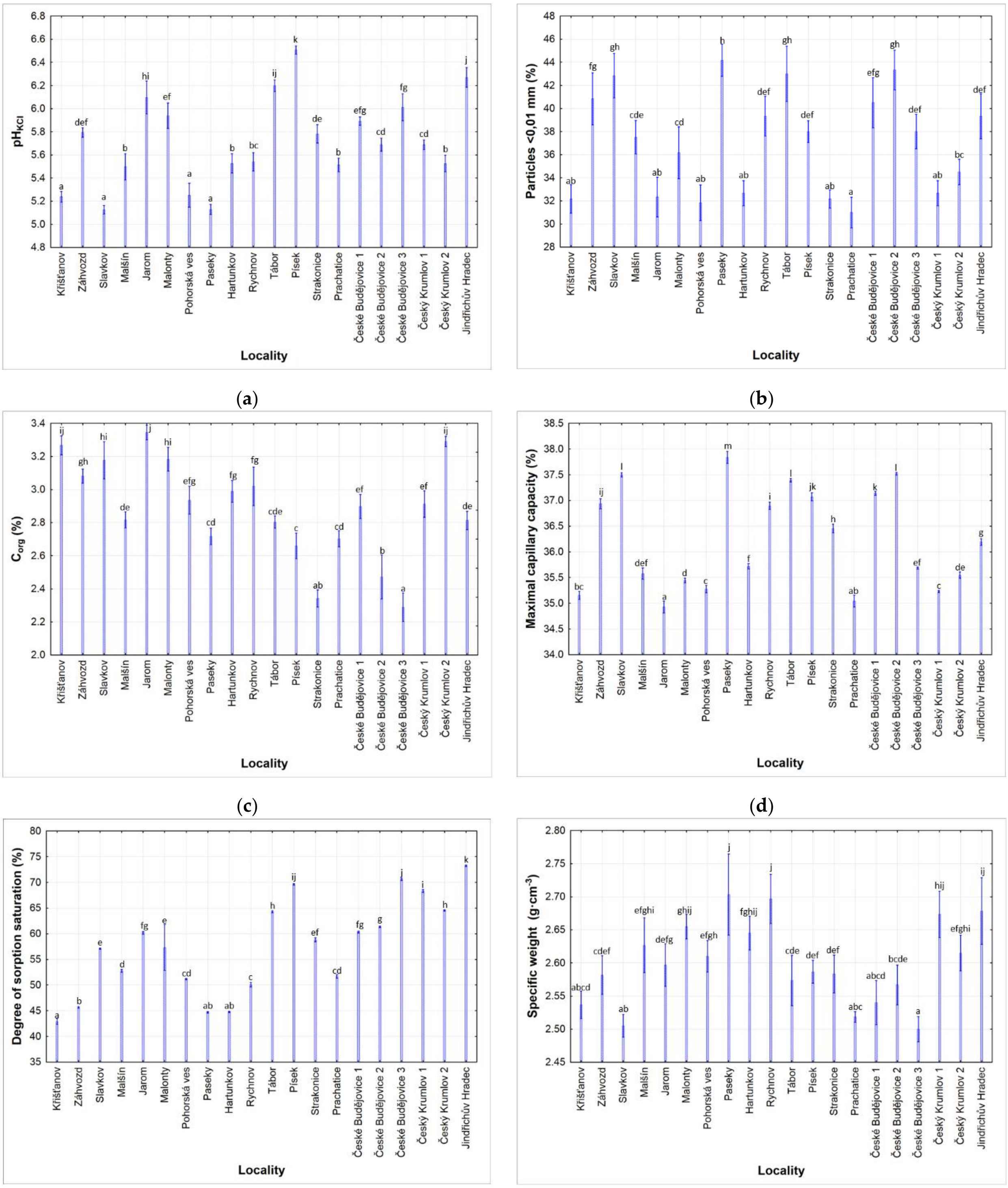
2.4. Determination of Free Light Fraction fLFOM, Occluded Light Fraction oLFOM, and Heavy Fraction DFOM of Soil Organic Matter

This determination was performed according to the method suggested by Balesdent et al. [54] and Golchin et al. [55]. The procedure for determining fLFOM was as follows: 10 g of sand-free soil samples (<2000 µm) was inserted into the centrifuge tube with 40 mL solution of sodium polytungstate at the density of 1.8 g/cm^3 (Sometu, Berlin, Germany). After shaking by hand, the suspension was allowed to stand for 30 min. Samples were then centrifuged (2000× *g*) for 30 min. The supernatant was vacuum filtered through a filter with pores <45 µm and then washed with 2000 mL of deionized water. After filtration, the amount of fLFOM was determined.

The remaining soil material in the centrifuge tube was then shaken on an orbital shaker (175 rpm/min) with ten 5 mm diameter glass beads with 40 mL of sodium polytungstate solution again at a density of 1.8 g/cm^3 for 18 h. After the first centrifugation and decantation, the soil particles were resuspended in 40 mL of polytungstate solution and centrifuged. This repeated procedure aims to completely separate the occluded light fraction oLF from the heavy fraction DF. The supernatants of both suspensions were combined and vacuum filtered. The remaining particles, corresponding to the heavy fraction DF with a density >1.8 g/cm^3, were washed with 1500 mL of deionized water to remove residual polytungstate. The suspension was then precipitated by adding 2.5 mL of 0.5M $AlCl_3$ per 1000 mL of supernatant and the supernatant was decanted with water. The heavy fraction DF was filtered off and washed with 500 mL of deionized water. This was followed by the carbon content determination in oLFOM and DFOM fractions.

2.5. Statistical Analysis

The data of Figures 1 and 2 were statistically evaluated by an analysis of variance (ANOVA) and the results were subsequently compared by a post-hoc Tukey HSD test. The method of principal component analysis (PCA) and factor analysis (FA) [56] was used for multivariate statistical analysis of measured data. Statistical analyses, including graphical outputs, were processed in STATISTICA (version 14, TIBCO Software, Inc., Palo Alto, CA, USA, 2021).



(**a**) (**b**)

(**c**) (**d**)

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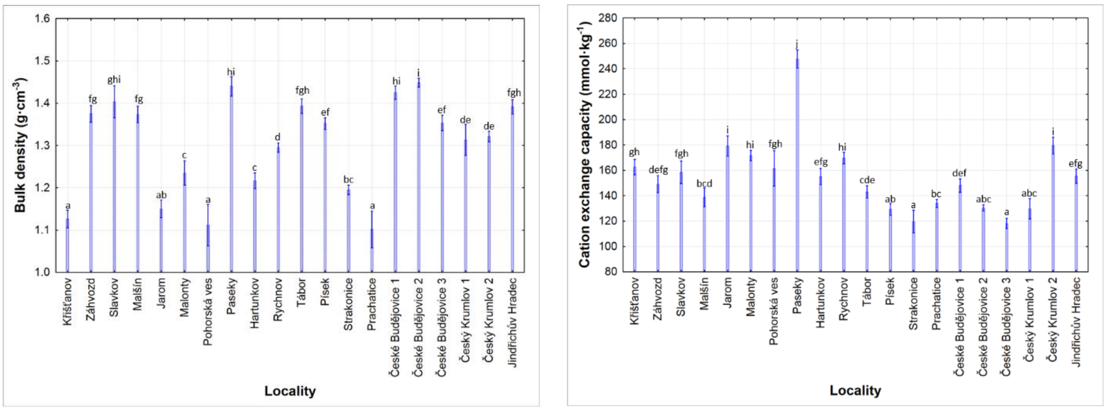
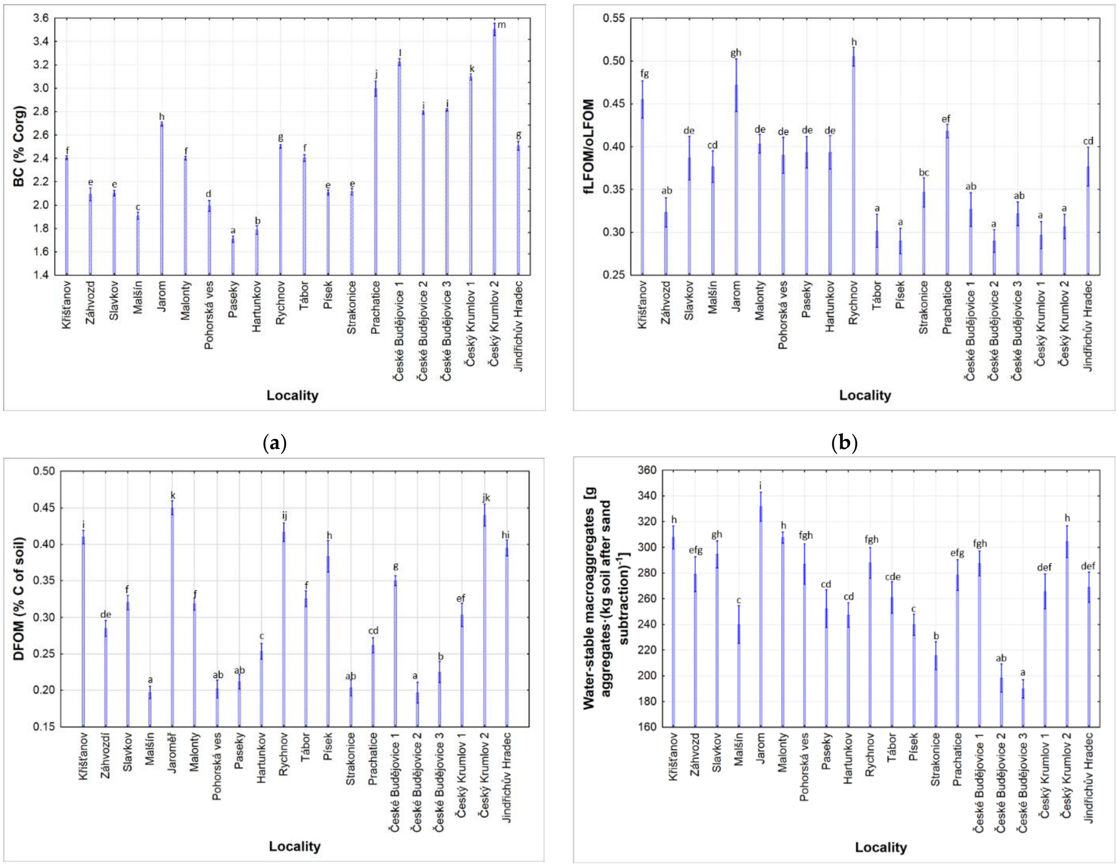
Figure 1. *Cont.*



(**g**) (**h**)

Figure 1. Analyses of samples of clay Cambisols (ANOVA, $p < 0.00001$): (**a**) pH_{KCl} ($F_{(19, 100)} = 161.38$); (**b**) particles <0.01 mm ($F_{(19, 100)} = 48.726$); (**c**) C_{org} ($F_{(19, 100)} = 111.06$); (**d**) maximal capillary capacity ($F_{(19, 100)} = 1136.8$); (**e**) degree of sorption saturation ($F_{(19, 100)} = 535.19$); (**f**) specific weight ($F_{(19, 100)} = 24.979$); (**g**) bulk density ($F_{(19, 100)} = 143.02$); (**h**) cation exchange capacity ($F_{(19, 100)} = 118.67$); significant differences between localities are shown in letters (Tukey's honest significance test; $p = 0.05$). Note: C_{org}—soil organic carbon (%).



(**a**) (**b**)

(**c**) (**d**)

Figure 2. Amounts of soil organic matter fractions monitored in samples of clay Cambisols (ANOVA, $p < 0.00001$): (**a**) Black carbon; (**b**) the ratio of free light fraction and the occluded light fraction of soil organic matter; (**c**) the organic matter of the heavy soil fraction; (**d**) water-stable macroaggregates. Note: BC—black carbon ($F_{(19, 100)} = 1494.3$); fLFOM/oLFOM—the ratio of free light fraction and the occluded light fraction of soil organic matter ($F_{(19, 100)} = 76.991$); DFOM—the organic matter of the heavy soil fraction ($F_{(19, 100)} = 343.35$). Water-stable macroaggregates ($F_{(19, 100)} = 69.371$); significant differences between localities are shown in letters (Tukey's honest significance test; $p = 0.05$).

3. Results and Discussion

3.1. Soil Properties

The average results (including standard deviations) of all monitored soil characteristics are summarized in Table S1. Soil analysis proved that clay Cambisols from experimental localities corresponds to average values in the Czech Republic. The specific gravity of the examined soils is in the range of 2.48–2.76 g/cm^3, which corresponds to the surface humus horizons. The bulk density is slightly lower (1.05–1.47 g/cm^3) than would correspond to clay topsoil (1.34–1.40 g/cm^3). The content of clay particles <0.01 mm is in the range of 30–45% for all samples, which corresponds to clay soils. The maximum capillary capacity is slightly higher than that of topsoil of clay soils (35%), probably due to the relatively high content of C_{org}, which here reaches the category of "excellent" (2.9%). Cation exchange capacity should be high in these high carbon soils. However, for most samples, it is only medium (130–240 mmol/kg soil), probably due to the higher acidity of all samples, corresponding to the category of weakly acidic to acidic soils (5.1–6.5 pH_{KCl}). For the same reason, the degree of sorption saturation is only medium (50–75%) or even lower. The results of the analyses of soil samples are summarized in Figure 1.

3.2. Black Carbon Content

Important results concerning soil organic matter are summarized in Figure 2. Samples of soils from relatively cleaner localities in southern Bohemia showed on average lower BC content (2.16% C_{org}) than samples with higher deposition of atmospheric fallout (2.76% C_{org}). These samples from sites with higher atmospheric pollution probably have BC of anthropogenic origin (ABC), i.e., unburned residues of industrial and local furnaces and emissions from transport, especially soot from unadjusted diesel engines. The study of historical sources did not prove the existence of recorded large fires in any of the experimental sites. Thus, it is clear that the group of samples from "clean" sites contains ancient historical BC (HBC), which can be partially oxidized over a long period of storage in the soil. As a result, its properties, especially sorption and ion exchange, will differ from relatively young, anthropogenic BC soils from atmospherically contaminated areas. In general, however, it can be stated that the amount of BC found in the whole experiment is meagre.

The finding of low BC values could be caused either by the chosen analytical method or by the used purification operations. BC analysis is generally considered very problematic because the analyst does not have a chemical individual, but always a very varied mixture. Although there are modern methods for determining BC in soils [21,36], in addition to demanding instrumental techniques, it is always necessary to use indirect relationships to calculate BC content in soils. The method of Kuhlbusch and Crutzen [20] was used in this research because BC defines unambiguously. In our opinion, the cleaning operations used could affect the correctness of the results, but not the accuracy. As this is a comparative work, we believe that the final evaluation of the cleaning operation will not be affected.

The average amount of soil organic matter DFOM in the heavy fraction DF in the soils is a precondition for higher contamination by atmospheric fallout (0.3083%) almost identical to in soils less contaminated (0.3397%). However, its relation correlates with the BC content ($r = 0.899268$), and with the ratio of free light fraction and the occluded light fraction of soil organic matter (fLFOM/oLFOM) ($r = 0.644752$) in localities without deposition. In localities with deposition, the relationship to BC is not correlated. This is evidence that long-lived HBC is strongly bound to the mineral colloidal soil fraction and, of course, to the less stable LFOM. On the contrary, the "young" ABC has not yet stably bound to mineral colloids, either because ABC (from traffic, resulting from the combustion of fuels in furnaces), is less stable than HBC from biomass fires, or it has not yet oxidized in the soil [57]. Therefore, no negatively charged carboxyl sites and other functional groups have formed on its surface, and therefore this ABC has only a sorption ability, not an ion exchangeability. For the firm connection of the mineral colloidal clay fraction with the colloidal organic fraction, the ion-exchange capacity is more important than the sorption capacity. By analogy, soil aggregates are much easier to form by combining mineral colloids with humic acid colloids than connecting them with soil non-humidified organic matter [13,14].

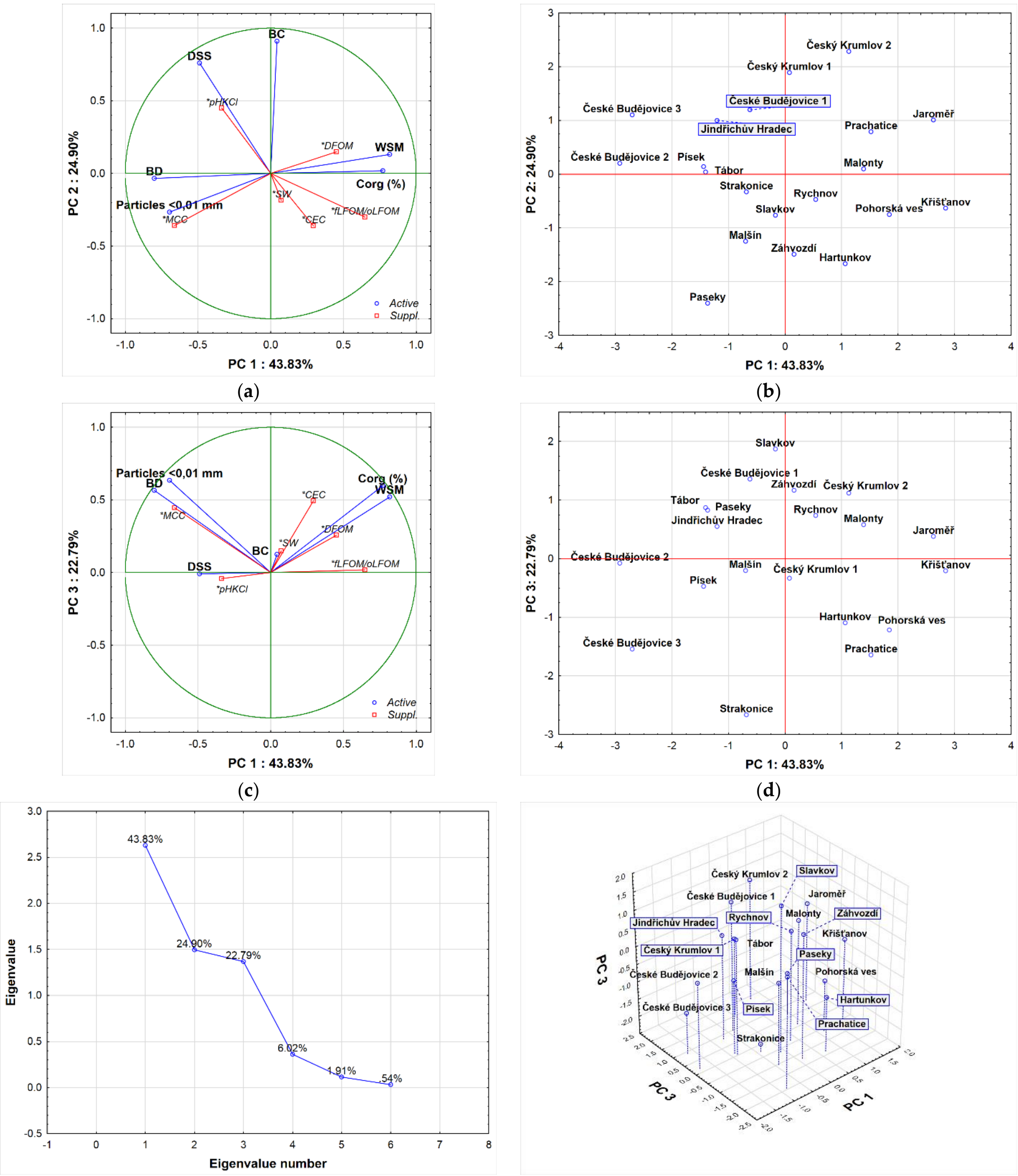
Anthropogenic BC, which does not affect DFOM in the heavy soil fraction of DF, forces the hypothesis that it will more easily undergo mineralization destruction in soil [22]. Therefore, it is necessary to take a general idea of the exceptional stability of BC in soil with some reserve [4,24].

On the other hand, it was found that the ratio of free light fraction and the occluded light fraction of soil organic matter correlates with BC content only in localities without deposition. In contrast, in localities with deposition, this relationship does not exist. This is confirmed by the conclusion of the previous paragraph and the finding that HBC is also bound in a light fraction of soil organic matter. As this ratio decreases in deposition sites, it is clear that the high sorption capacity of ABC leads to the formation of an occluded light fraction of oLFOM soil organic matter. It is a stabilizing mechanism [13]. Nevertheless, although fLFOM is more labile than oLFOM. However, oLFOM also mineralizes in the soil in the order of decades [12]. Therefore, ABC cannot be a pool of permanently stored carbon in the soil.

Correlation analysis revealed a close relationship between the BC content in the soil and the number of water-stable aggregates. In localities with atmospheric fallout deposition, this relationship is less significant. The formation of water-resistant macroaggregates is a much less sensitive indicator than the fLFOM/oLFOM ratio. Therefore, this result is not surprising; it only confirms the conclusion of the previous paragraph [50]. BC did not contribute to the higher forms of the occluded light fraction of organic matter within the aggregates and thus did not positively affect their amount [51]. This may be due to this phenomenon: BC, which has both sorption and ion exchange properties (HBC), is low in soil and is diluted in sites with ABC deposition (which has only sorption properties). Anthropogenic BC is not yet oxidized, having no negative charge network on its surface [29]. Therefore, there was no sorption of foreign, oxidized organic soil matter [33] and thus no increase in CEC [34]. The soils from both groups of localities had the same CEC. The dilution of "quality" HBC by "poor quality" ABC and other influences caused even higher CEC in soils from atmospherically cleaner localities, with lower BC content. Thus, the C_{org} content in samples of localities with higher deposition of atmospheric fallout correlates more significantly ($r = 0.840711$) with CEC than in samples from localities without deposition ($r = -0.310164$).

3.3. Evaluation of Results from the Point of View Principal Component Analysis and Factor Analysis

On the graph of component weights PC1, PC2, PC3 (Figure 3), the first two axes are significant, which together exhaust about 92% of the variability. The PC1 axis in the PC1 × PC2 graph unambiguously characterizes WSM and BD, which go directly along this axis and are correlated with it at a level exceeding 0.81 and −0.80 (high correlation), as well as C_{org} ($r = 0.77$) and particles 0.01 ($r = -0.69$). On the PC2 axis, there is a significant correlation between BC and DSS ($r = 0.91$ and 0.75). There is no significant correlation on the PC3 axis, but the direction is differentiated according to particles 0.01 ($r = 0.63$) and C_{org} ($r = 0.59$).



(**a**) (**b**) (**c**) (**d**) (**e**) (**f**)

Figure 3. Principal component analysis (PCA) of soil quality parameters in the area of interest: (**a**) graph of component weights 1 a 2 (PC1 × PC2) for soil quality parameters. (**b**) The scatterplot of the component score PC1 × PC2 for individual localities. (**c**) Graph of component weights 1 a 3 (PC1 × PC3) for soil quality parameters. (**d**) The scatterplot of the component score PC1 × PC3 for individual localities. (**e**) Scree plot; (**f**) 3D graph PC1 × PC2 × PC3 for individual localities. Note: BC—black carbon (% C_{org}); fLFOM/oLFOM—the ratio of free light fraction and the occluded light fraction of soil organic matter; DFOM—the organic matter of the heavy soil fraction (% C of soil); WSM—water-stable macroaggregates (g aggregates (kg soil after sand subtraction)$^{-1}$); CEC—cation exchange capacity (mmol/kg); pH_{KCl}—soil reaction; particles <0.01 mm—clay particles; C_{org}—soil organic carbon (%); MCC—maximal capillary capacity (%); SW—specific weight (g/cm^3); DSS—degree of sorption saturation (%); BD—bulk density (g/cm^3).

In the scatterplot of the component score, sampling sites according to WSM, C_{org}, BD and particles are clearly located along the PC1 axis. The PCA divided the places in the area of interest into several different clusters. The cluster of localities České Budějovice 2 and 3 are characterized by a very high content of DSS, a higher BD and the lowest content of WSM and C_{org} (also distinguished in the graph PC1 × PC3) and a higher content of BC. On the contrary, the localities Jaroměř and Křišťanov are characterized by the highest content of WSM, C_{org} and the lowest BD and very similar content of particles. The Paseky and Hartunkov localities deviate from other localities with the lowest BC content (1.70–1.78%). The Český Krumlov 2 locality has the highest BC content (3.50%) with a high C_{org} content (3.29%). Therefore, these two localities are at the most significant distance from each other within the PCA axis. Other localities have similar soil quality parameters and, thus, form the largest cluster around the center. The Strakonice locality with the PC1 × PC3 graph also differed significantly from other localities with a low content of BC (2.11%) and C_{org} (2.34%).

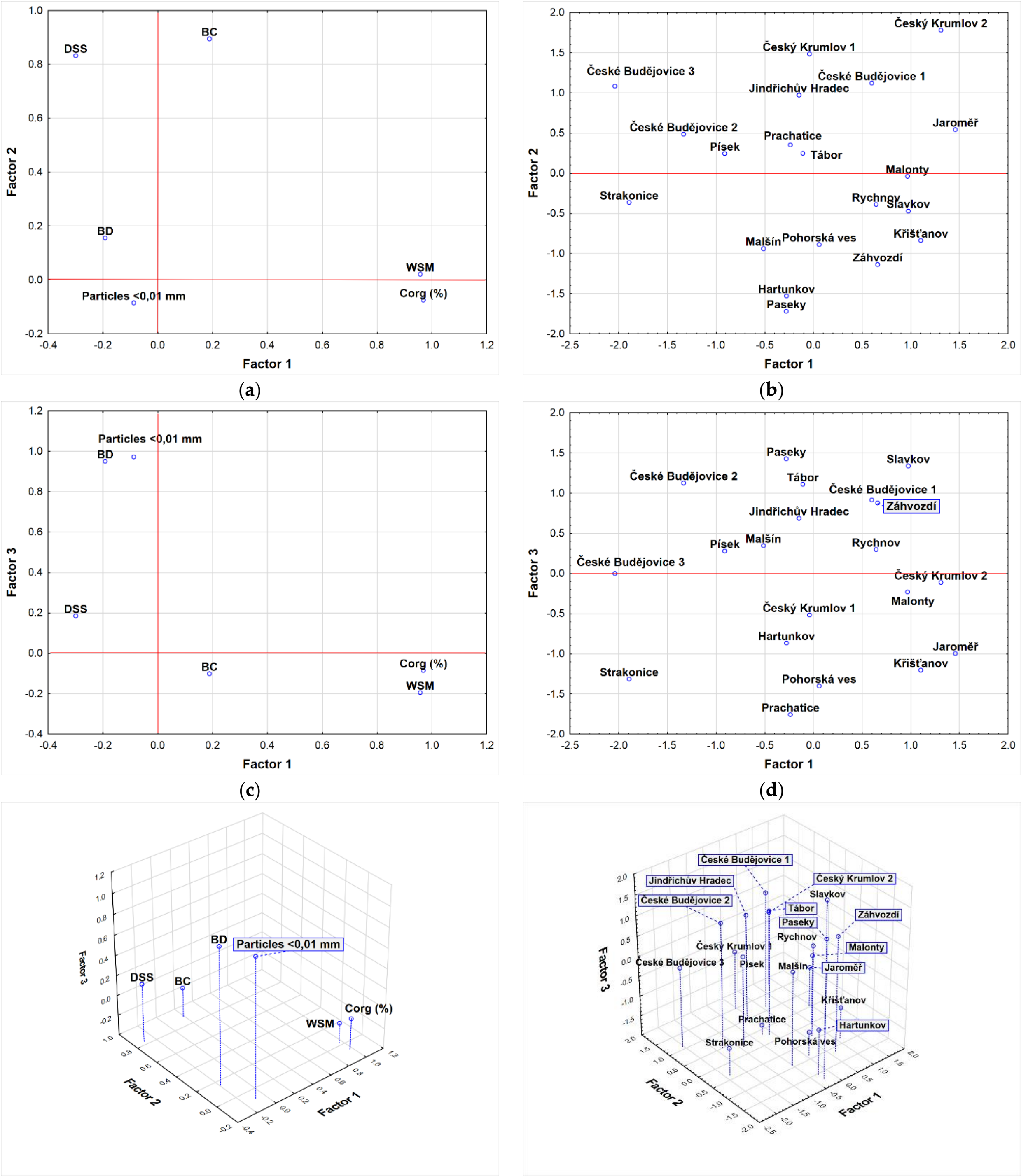
Factor analysis (FA) (Figure 4) confirmed the results of PCA and differentiated similarly to the PCA method of the group of localities (see scattering diagrams of component scores). Factor weights explain the correlations between factors and features. They represent essential information on which the interpretation of factors is based. Factor 1 describes the properties in terms of C_{org} and WSM. The cluster of localities České Budějovice 2, 3, and Strakonice are characterized by the lowest content of WSM and C_{org}, on the contrary, the localities Jaroměř and Křišťanov have the highest range of WSM, C_{org}. Factor 2 clearly describes the content of BC and DSS. The lowest BC content was determined in the Paseky and Hartunkov localities. Therefore, they are differentiated from other localities in the Factor 1 × Factor 2 graph, within the factor 2 axis. Factor 3 describes BD and particles. The Paseky locality has the highest BD and particles, while the Prachatice locality has the lowest BD and particles. Communality represents the proportion of character variability expressed by the factors in question. It is similar to the value of R^2, which we obtain when the original characters are explained by regression by selected factors [56]. From the contribution of Factor 1, Factor 2, and Factor 3 to communality, it is clear how communality acquires high values. Thus, the features of most values are very well considered by the proposed factor model (Table 1).

Table 1. Factor weights and contributions of a given factor to the communality for individual traits after rotation of varimax normalized soil quality parameters in the area of interest.

Parameter	Factor Weight			Contributions of a Given Factor to the Communality			
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3	Communalities
BC	0.1885	0.8944	−0.1017	0.0355	0.8355	0.8458	0.4384
BD	−0.1917	0.1561	0.9496	0.0368	0.0611	0.9628	0.9087
DSS	−0.2992	0.8325	0.1843	0.0895	0.7827	0.8166	0.5265
C_{org}	0.9692	−0.0750	−0.0854	0.9393	0.9449	0.9522	0.8948
WSM	0.9578	0.0212	−0.1946	0.9173	0.9178	0.9556	0.9084
Particles < 0.01 mm	−0.0876	−0.0849	0.9715	0.0077	0.0149	0.9586	0.8845

Note: BC—black carbon (% C_{org}); BD—bulk density (g/cm^3); DSS—degree of sorption saturation (%); C_{org}—soil organic carbon (%); WSM—water-stable macroaggregates (g aggregates·(kg soil after sand subtraction)$^{-1}$); particles < 0.01 mm—clay particles (%).

Multidimensional statistical methods (multicriteria evaluation using PCA and FA methods) significantly enabled, based on extensive data analysis, to differentiate the area of interest in the evaluated parameters (WSM, C_{org}, BC, etc.) into different clusters (individual localities within differentiated clusters have their own qualitative parameters soils very similar).



(**a**) (**b**)

(**c**) (**d**)

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Figure 4. Factor analysis (FA) of soil quality parameters in the area of interest: (**a**) graph of factor weights (Factor 1 × Factor 2) for soil quality parameters. (**b**) Scattering diagram of component scores Factor 1 × Factor 2 for individual localities. (**c**) Graph of factor weights (Factor 1 × Factor 3) for soil quality parameters; (**d**) scattering diagrams of component score Factor 1 × Factor 3 for individual localities; (**e**) 3D graph Factor 1 × Factor 2 × Factor 3 for soil quality parameters; (**f**) 3D graph Factor 1 × Factor 2 × Factor 3 for individual localities. Note: BC—black carbon (% C_{org}); fLFOM/oLFOM—the ratio of free light fraction and the occluded light fraction of soil organic matter; WSM—water-stable macroaggregates (g aggregates·(kg soil after sand subtraction)$^{-1}$); particles < 0.01 mm—clay particles; C_{org}—soil organic carbon (%); DSS—degree of sorption saturation (%); BD—bulk density (g/cm^3).

4. Conclusions

Organic matter influences the soil ecosystem and, indirectly, the environment. One of the important fractions of soil organic matter is black carbon. Therefore, this study investigated black carbon in the clay Cambisols with its different atmospheric fallout. On average, lower black carbon content was found in sparsely populated areas of southern Bohemia (2.16% C_{org}). In comparison, it was higher in areas of larger cities with a significant anthropogenic load (2.76% C_{org}). Black carbon in the soils of larger cities probably has an anthropogenic origin. Thus, two types of black carbon were found. The first one is historical from biomass fire when the second one is anthropogenic and relatively new. It is created from combustion in furnaces and transport fumes, and does not significantly affect organic matter. However, both groups of black carbon have entirely different properties and effects on the environment. Historical black carbon from atmospherically cleaner localities is firmly bound with mineral soil colloids. It is evident from the relationship of its content in the soil to the heavy fraction of soil organic matter; moreover, from the ratio of free light fraction and the occluded light fraction of soil organic matter. On the contrary, in soils from localities loaded by atmospheric fallout, the relationship of black carbon content to these parameters is negligible. Thus, it can therefore be stated that anthropogenic black carbon is much less stable in soils than historical black carbon because it has not yet been associated with mineral colloids. This is because its chemical properties are entirely different from historical black carbon or has not been oxidized in soils yet. That is why anthropogenic black carbon has only the sorption capacity, not the cation exchange capacity, in contrast with historical black carbon. The high sorption capacity of anthropogenic black carbon leads to forming an occluded light fraction of soil organic matter, which is a stabilizing mechanism, although very slow. The free light fraction of soil organic matter is less stable than the occluded fraction. However, even the occluded fraction mineralizes in the soil for decades, so anthropogenic black carbon cannot be a pool of permanently stored carbon in the soil.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/agronomy11112261/s1, Table S1: Basic descriptive statistics; Figure S1: The map of sampling localities (South Bohemia, Czech Republic).

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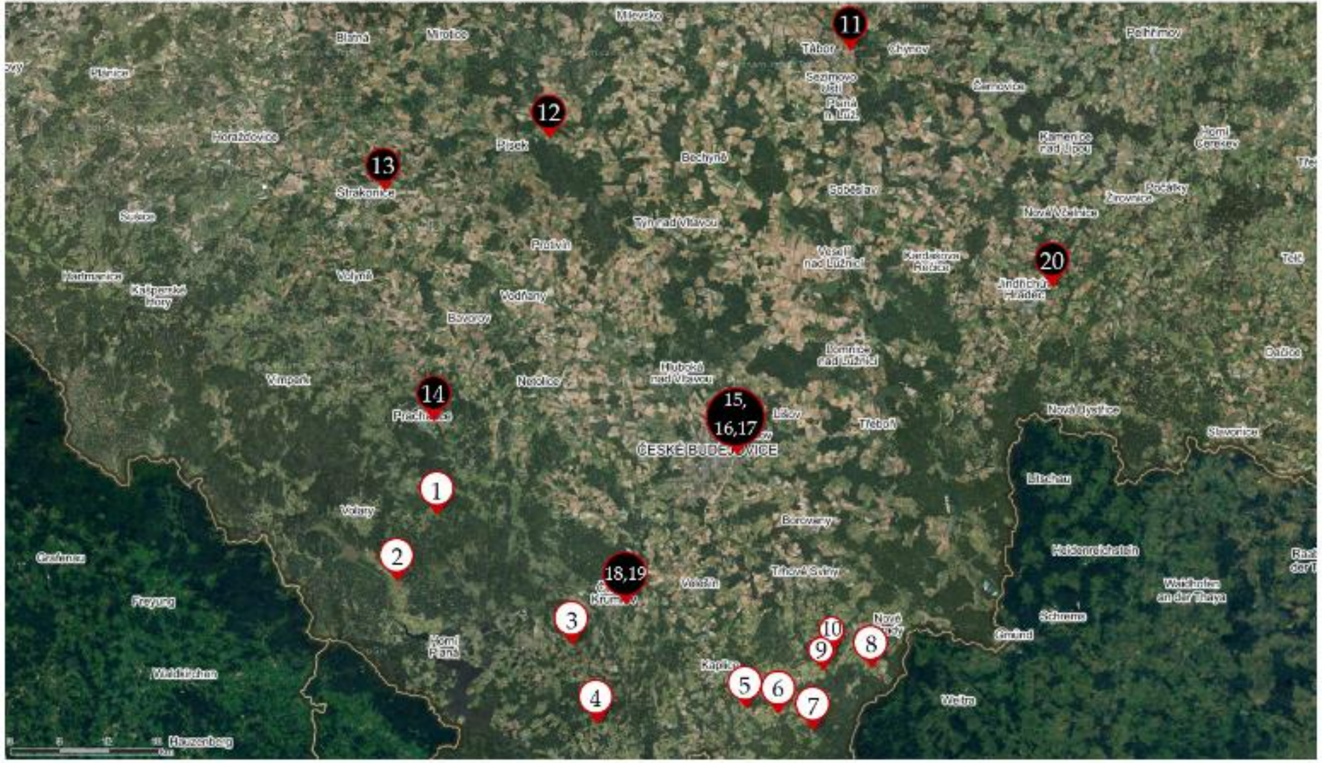
Figure S1. The map of sampling localities (South Bohemia, Czech Republic).



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Note: 1—Křišťanov; 2—Záhvozí; 3—Slavkov; 4—Malšín; 5—Jaroměř; 6—Malonty; 7—Pohorská ves; 8—Paseky; 9—Hartunkov; 10—Rychnov; 11—Tábor; 12—Písek; 13—Strakonice; 14—Prachatice; 15—České Budějovice 1; 16—České Budějovice 2; 17—České Budějovice 3; 18—Český Krumlov 1; 19—Český Krumlov 2; 20—Jindřichův Hradec. The source of the map background is the Mapy.cz website.

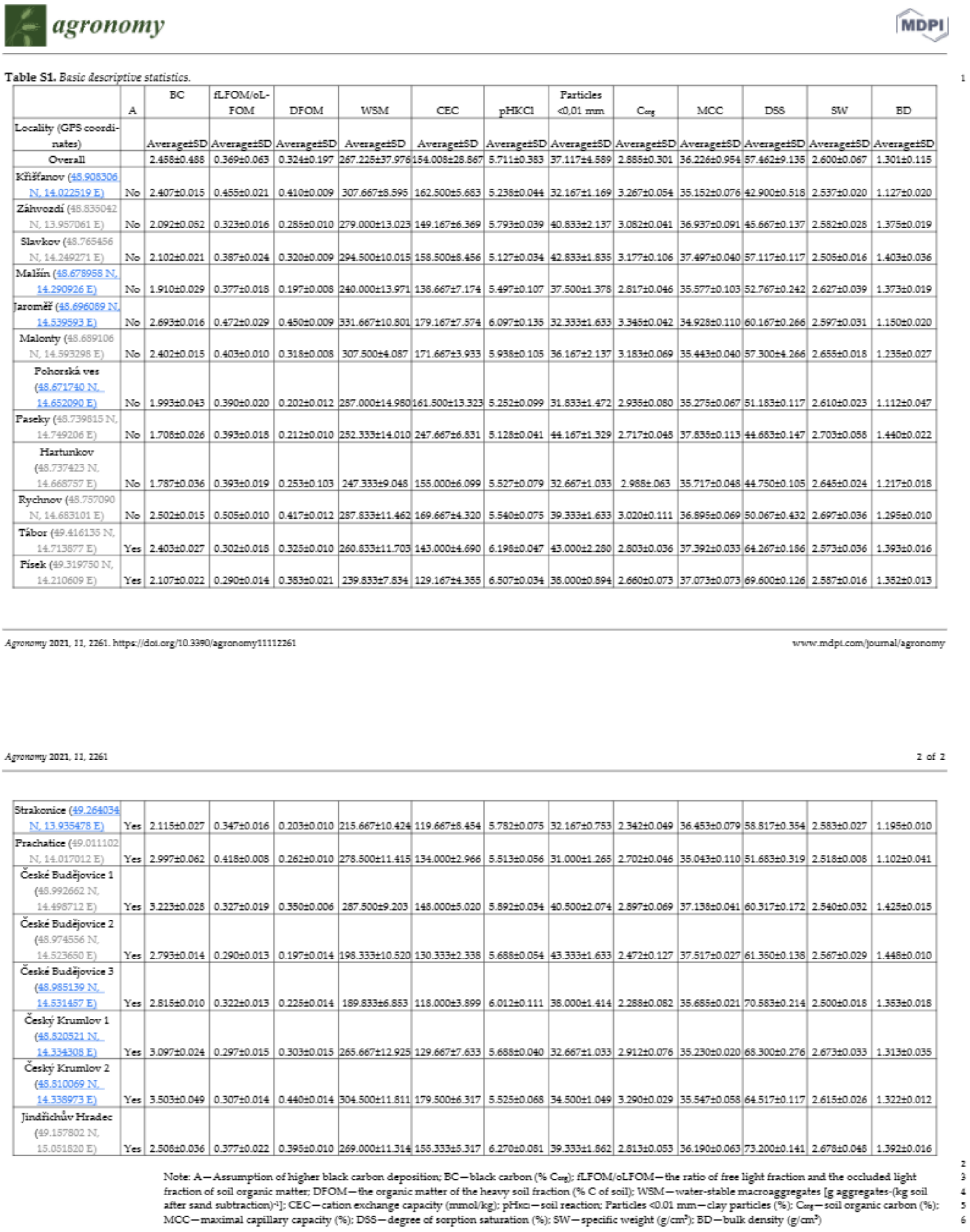

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Table S1. *Basic descriptive statistics.*

	A	BC	fLFOM/oLFOM	DFOM	WSM	CEC	pHKCl	Particles <0,01 mm	C_{org}	MCC	DSS	SW	BD
Locality (GPS coordinates)		Average±SD	Average±SD	Average±SD	Average±SD	Average±SD	Average±SD	Average±SD	Average±SD	Average±SD	Average±SD	Average±SD	Average±SD
Overall		2.458±0.488	0.369±0.063	0.324±0.197	267.225±37.976	154.008±28.867	5.711±0.383	37.117±4.589	2.885±0.301	36.226±0.954	57.462±9.135	2.600±0.067	1.301±0.115
Křišťanov (48.908306 N, 14.022519 E)	No	2.407±0.015	0.455±0.021	0.410±0.009	307.667±8.595	162.500±5.683	5.238±0.044	32.167±1.169	3.267±0.054	35.152±0.076	42.900±0.518	2.537±0.020	1.127±0.020
Záhvozdí (48.835042 N, 13.957061 E)	No	2.092±0.052	0.323±0.016	0.285±0.010	279.000±13.023	149.167±6.369	5.793±0.039	40.833±2.137	3.082±0.041	36.937±0.091	45.667±0.137	2.582±0.028	1.375±0.019
Slavkov (48.765456 N, 14.249271 E)	No	2.102±0.021	0.387±0.024	0.320±0.009	294.500±10.015	158.500±8.456	5.127±0.034	42.833±1.835	3.177±0.106	37.497±0.040	57.117±0.117	2.505±0.016	1.403±0.036
Malšín (48.678958 N, 14.290926 E)	No	1.910±0.029	0.377±0.018	0.197±0.008	240.000±13.971	138.667±7.174	5.497±0.107	37.500±1.378	2.817±0.046	35.577±0.103	52.767±0.242	2.627±0.039	1.373±0.019
Jaroměř (48.696089 N, 14.539593 E)	No	2.693±0.016	0.472±0.029	0.450±0.009	331.667±10.801	179.167±7.574	6.097±0.135	32.333±1.633	3.345±0.042	34.928±0.110	60.167±0.266	2.597±0.031	1.150±0.020
Malonty (48.689106 N, 14.593298 E)	No	2.402±0.015	0.403±0.010	0.318±0.008	307.500±4.087	171.667±3.933	5.938±0.105	36.167±2.137	3.183±0.069	35.443±0.040	57.300±4.266	2.655±0.018	1.235±0.027
Pohorská ves (48.671740 N, 14.652090 E)	No	1.993±0.043	0.390±0.020	0.202±0.012	287.000±14.980	161.500±13.323	5.252±0.099	31.833±1.472	2.935±0.080	35.275±0.067	51.183±0.117	2.610±0.023	1.112±0.047
Paseky (48.739815 N, 14.749206 E)	No	1.708±0.026	0.393±0.018	0.212±0.010	252.333±14.010	247.667±6.831	5.128±0.041	44.167±1.329	2.717±0.048	37.835±0.113	44.683±0.147	2.703±0.058	1.440±0.022
Hartunkov (48.737423 N, 14.668757 E)	No	1.787±0.036	0.393±0.019	0.253±0.103	247.333±9.048	155.000±6.099	5.527±0.079	32.667±1.033	2.988±.063	35.717±0.048	44.750±0.105	2.645±0.024	1.217±0.018
Rychnov (48.757090 N, 14.683101 E)	No	2.502±0.015	0.505±0.010	0.417±0.012	287.833±11.462	169.667±4.320	5.540±0.075	39.333±1.633	3.020±0.111	36.895±0.069	50.067±0.432	2.697±0.036	1.295±0.010
Tábor (49.416135 N, 14.713877 E)	Yes	2.403±0.027	0.302±0.018	0.325±0.010	260.833±11.703	143.000±4.690	6.198±0.047	43.000±2.280	2.803±0.036	37.392±0.033	64.267±0.186	2.573±0.036	1.393±0.016
Písek (49.319750 N, 14.210609 E)	Yes	2.107±0.022	0.290±0.014	0.383±0.021	239.833±7.834	129.167±4.355	6.507±0.034	38.000±0.894	2.660±0.073	37.073±0.073	69.600±0.126	2.587±0.016	1.352±0.013
Strakonice (49.264034 N, 13.935478 E)	Yes	2.115±0.027	0.347±0.016	0.203±0.010	215.667±10.424	119.667±8.454	5.782±0.075	32.167±0.753	2.342±0.049	36.453±0.079	58.817±0.354	2.583±0.027	1.195±0.010
Prachatice (49.011102 N, 14.017012 E)	Yes	2.997±0.062	0.418±0.008	0.262±0.010	278.500±11.415	134.000±2.966	5.513±0.056	31.000±1.265	2.702±0.046	35.043±0.110	51.683±0.319	2.518±0.008	1.102±0.041
České Budějovice 1 (48.992662 N, 14.498712 E)	Yes	3.223±0.028	0.327±0.019	0.350±0.006	287.500±9.203	148.000±5.020	5.892±0.034	40.500±2.074	2.897±0.069	37.138±0.041	60.317±0.172	2.540±0.032	1.425±0.015
České Budějovice 2 (48.974556 N, 14.523650 E)	Yes	2.793±0.014	0.290±0.013	0.197±0.014	198.333±10.520	130.333±2.338	5.688±0.054	43.333±1.633	2.472±0.127	37.517±0.027	61.350±0.138	2.567±0.029	1.448±0.010
České Budějovice 3 (48.985139 N, 14.531457 E)	Yes	2.815±0.010	0.322±0.013	0.225±0.014	189.833±6.853	118.000±3.899	6.012±0.111	38.000±1.414	2.288±0.082	35.685±0.021	70.583±0.214	2.500±0.018	1.353±0.018
Český Krumlov 1 (48.820521 N, 14.334308 E)	Yes	3.097±0.024	0.297±0.015	0.303±0.015	265.667±12.925	129.667±7.633	5.688±0.040	32.667±1.033	2.912±0.076	35.230±0.020	68.300±0.276	2.673±0.033	1.313±0.035
Český Krumlov 2 (48.810069 N, 14.338973 E)	Yes	3.503±0.049	0.307±0.014	0.440±0.014	304.500±11.811	179.500±6.317	5.525±0.068	34.500±1.049	3.290±0.029	35.547±0.058	64.517±0.117	2.615±0.026	1.322±0.012
Jindřichův Hradec (49.157802 N, 15.051820 E)	Yes	2.508±0.036	0.377±0.022	0.395±0.010	269.000±11.314	155.333±5.317	6.270±0.081	39.333±1.862	2.813±0.053	36.190±0.063	73.200±0.141	2.678±0.048	1.392±0.016

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Note: A—Assumption of higher black carbon deposition; BC—black carbon (% C_{org}); fLFOM/oLFOM—the ratio of free light fraction and the occluded light fraction of soil organic matter; DFOM—the organic matter of the heavy soil fraction (% C of soil); WSM—water-stable macroaggregates [g aggregates·(kg soil after sand subtraction)$^{-1}$]; CEC—cation exchange capacity (mmol/kg); pH_{KCl}—soil reaction; Particles <0.01 mm—clay particles (%); C_{org}—soil organic carbon (%); MCC—maximal capillary capacity (%); DSS—degree of sorption saturation (%); SW—specific weight (g/cm^3); BD—bulk density (g/cm^3)

4 Biochar jako půdní pomocná látka

V předchozí části práce byla představena POH, objasněn její význam a vysvětleno její dělení. Existují tedy frakce relativně labilní a frakce relativně stabilní. Mezi nimi je samozřejmě možné nalézt určité mezistupně. Odborná literatura popisuje řadu možností, jak lze POH dělit z hlediska její stability. Tato kapitola tematicky navazuje na předchozí článek zabývající se takzvaným black carbonem. Následující text bude věnován aktuální a široce diskutované problematice – využití biocharu v zemědělství.

4.1 Co je to biochar?

Pro přehlednost je nutné nejdříve definovat, co pojem biochar znamená. Jak totiž udávají Bolan et al. (2022): „Biochar je black carbon, ale ne každý black carbon je biochar.“ Autoři vysvětlují, že biochar není jedinou entitou, ale spíše zahrnuje širokou škálu forem black carbonu. Terminologii black carbonu se podrobně věnují Jones et al. (1997). Pojem biochar však ještě ve svém přehledu zahrnutý nemají.

Dle Spokas et al. (2012) byl termín biochar poprvé použit pravděpodobně v roce 1998 a označoval pevný zbytek po pyrolýze biomasy. Laird et al. (2010) popisují biochar jako vedlejší produkt termochemické přeměny lignocelulózových materiálů na pokročilá biopaliva. Biochar je tedy zuhelnatělý materiál s velkým povrchem a bohatými funkčními skupinami (Glaser et al., 2002; Cheng et al., 2008). Ve velkém množství obsahuje uhlík, vodík a kyslík. Dalšími prvky jsou například dusík, síra, fosfor, draslík, hořčík, hliník, železo, vápník či křemík (Bolan et al., 2022).

Biochar vzniká pyrolýzou – termochemickým procesem (> 250 °C), při kterém dochází za nepřístupu kyslíku k rozkladu organického materiálu (Tsuge a Ohtani, 2011). Pyrolýza zahrnuje následující pochody. V první řadě jde o eliminaci vlhkosti. Následuje depolymerace a fragmentace lignocelulózových materiálů spolu s eliminací CO_2 a vázané vody. Třetím krokem je re-kondenzace a repolymerace vedoucí k uhelnatění (Foong et al., 2020). Kromě biocharu jsou produktem pyrolýzy zejména pyrolýzní plyny a také pyrolýzní olej (Soni a Karmee, 2020). Substrátem pro výrobu biocharu mohou být kromě rostlinných zbytků také mrtvá těla zvířat, hnůj, potravinářský, biologický či komunální odpad (Purakayastha et al., 2019).

V důsledku selektivního odstraňování organických molekul a změn původní uhlíkové struktury má biochar výrazně vyšší specifický povrch, pórovitost a odolnost proti biologické degradaci než výchozí biomasa (Leng et al., 2020; Zimmerman, 2010). V půdě by tedy měl být velmi stabilní (Kuzyakov et al., 2009; Kuzyakov et al., 2014). Někteří autoři proto začali spojovat termín biochar s pevným produktem pyrolýzy, který je vyroben speciálně pro účely sekvestrace uhlíku (např. Lehmann, 2007). Vysokou stabilitu biocharu v půdě však částečně zpochybňují Yang et al. (2022), kteří ve svých experimentech zkoumali stabilitu biocharu v závislosti na půdních vlastnostech.

4.2 Využití a účinky biocharu

Biochar neslouží v půdě jen jako prostředek pro uchování uhlíku (Lehmann, 2007; Parthasarathy et al., 2022), ale také jako pomocná látka pro zlepšení kvality půdy (Githinji, 2014), což je z pohledu zemědělce hlavní motivací pro jeho aplikaci na pole (Kalu et al., 2021). Výzkumy dokázaly, že aplikace biocharu vedla ke zlepšení mnoha výnamných půdních vlastností i zvýšení výnosu pěstovaných plodin.

Biochar má přímý vliv na fyzikální vlastnosti půdy. Uvádí se, že po aplikaci biocharu na půdu dochází ke snížení objemové hmotnosti (Mandal et al., 2018; Yan et al., 2019), podpoře tvorby půdních agregátů (Zhang et al., 2020a) a lepšímu zadržování vody (Kambo a Dutta 2015; Razzaghi et al., 2020; Ścisłowska et al., 2015). Jsou známy i studie popisující biochar jako látku, která má pozitivní vliv na mikrobiální společenstva a zvýšení biologické aktivity (Lehmann et al., 2011; Mandal et al., 2018; Meier et al., 2019). Účinky biocharu byly potvrzeny také při úpravě půdní reakce (Domingues et al., 2017; Laghari et al., 2016; Mukherjee a Lal, 2013). Významný vliv na půdní úrodnost je připisován rovněž pozitivnímu vlivu biocharu na zvyšování kationtové výměnné kapacity půdy (Farhangi-Abriz a Ghassemi-Golezani, 2023; Munera-Echeverri et al., 2018; Ścisłowska et al., 2015).

Biochar taktéž ovlivňuje živinný stav půdy. Lusiba et al. (2017) poukazují na to, že už samotná přítomnost biocharu v půdě má za následek změnu půdních vlastností, a tedy i koloběhu živin. Přímý vliv má pak dodání živin obsažených v biocharu (Haefele et al., 2011; Li et al., 2017). Biochar může být zdrojem dusíku, fosforu i draslíku (Purakayastha et al., 2019). Je ovšem třeba brát v úvahu, že část dusíku a síry z výchozích materiálů se ztratí plynnými emisemi během pyrolýzy (Al–Wabel et al., 2013; Leng et al., 2020). Dále jsou v biocharu obsaženy vápník, hořčík a stopové prvky vyskytující se v původní surovině (Chen et al., 2018; Flavel a Murphy, 2006; Quilty a Cattle, 2011) a během zvětrávání biocharu se stávají dostupnými pro rostliny (Zhao et al., 2018). Díky tomu, že biochar dokáže živiny také poutat, se snižují jejich ztráty vyluhováním (Singh et al., 2010) či plynnými emisemi (Thangarajan et al., 2018).

Pozitivní vlastnosti biocharu shrnují Bolan et al. (2022). Biochar označují za multifunkční nástroj, který je vhodný pro úpravu půdy, pro zlepšení zdraví půdy, funguje jako nosič živin, imobilizační činidlo pro sanaci toxických kovů a organických kontaminantů i pro zmírnění emisí skleníkových plynů.

4.3 Rizika spojená s aplikací biocharu

Zatímco dříve byl v odborné literatuře biochar často nekriticky doporučován jako výborný půdní kondicionér, dnes se situace mění a autoři jsou si vědomi i úskalí, která s sebou výroba a použití biocharu v zemědělství přinášejí. Záleží totiž nejen na půdním druhu, typu a dalších lokálních podmínkách, ale také na původu biocharu. Jeho vlastnosti se liší na základě specifických podmínek pyrolýzy, jako je teplota, maximální teplota nebo čas (Mukherjee a Lal, 2013) a vstupním materiálu (Zhao et al., 2013). V závislosti na těchto parametrech může být výsledný produkt vysoce variabilní. Tématu kvality biocharu v závislosti na vstupních materiálech a podmínkách pyrolýzy se věnují například Hassan et al. (2020).

Ścisłowska et al. (2015) podotýkají, že účinky biocharu na půdu zůstávají poměrně neprozkoumané. Zhang et al. (2020b) upozorňují na složité vztahy na bázi rostlina-biochar-půda, protože účinky biocharu do značné míry závisejí na konkrétní půdě a jejím pH, dávce biocharu, pěstované rostlině atd. Nevhodná je aplikace biocharu na alkalické půdy (Azzi et al., 2019). Ačkoli množství studií reportuje o pozitivním vlivu biocharu na půdní edafon, Kochanek et al. (2022) se domnívají, že o této oblasti se ví velmi málo. Na změny ve složení mikrobiálního společenstva poukazují i Ducey et al. (2013). Dotčené může být i společenstvo rostlin (Kochanek et al., 2022).

Ekonomickou stránkou aplikace biocharu se zabývali například Maroušek et al. (2015), Maroušek et al. (2019), Thengane et al. (2020), Vochozka et al. (2016). Kolem ekonomiky trhu s biocharem přetrvává nejistota (Van Fan et al., 2021; Maroušek et al., 2019; Roy a Dias, 2017).

S množstvím pozitivních účinků biocharu jsou tedy spojena i určitá rizika. Vždy je nutné brát v úvahu fakt, že každý pevný produkt pyrolýzy může mít naprosto rozdílné vlastnosti. Prvním významným faktorem je vstupní surovina, neméně důležitý je i samotný pyrolytický proces, a dokonce i případná úprava vzniklého biocharu. Nelze nezmínit fakt, že i každá půda bude na aplikaci biocharu reagovat odlišně. Problematice výroby, vlastností a využití biocharu se věnuje následná série odborných publikací.

5 Komentované publikace autora – Část 2

Publikace 4: Vliv pyrolýzní teploty na vlastnosti biocharu a jeho efekt na půdní hydrologické podmínky

Ghorbani, M., Amirahmadi, E., Neugschwandtner, R. W., Konvalina, P., Kopecký, M., Moudrý, J., ... & Murindangabo, Y. T. (2022). The impact of pyrolysis temperature on biochar properties and its effects on soil hydrological properties. Sustainability, 14(22), 14722. DOI: 10.3390/su142214722.

Teplota pyrolýzy je jedním z hlavních faktorů, které ovlivňují vlastnosti vzniklého biocharu. Dále o účincích biocharu na půdu či rostliny rozhoduje také vstupní surovina a charakteristika půdy samotné. V tomto článku byly zkoumány biochary vyrobené z pšeničné slámy za různých teplot (350, 450, 550, 650 °C). Doba pyrolýzního procesu činila 120 minut. Testovanou půdou byla jílovitá luvizem, přičemž test probíhal v nádobových pokusech. Byl zkoumán vliv daných biocharů na vybrané půdní charakteristiky, zejména týkající se půdních hydrologických vlastností. Tato oblast výzkumu je vysoce aktuální. V souvislosti se změnami klimatu se předpokládá vyšší četnost a rozsah extrémních klimatických jevů, jako jsou silné srážky, záplavy a sucha v celé Evropě (Cacciotti et al., 2021). Naumann et al. (2021) předpokládají, že se změní distribuce vody v čase a prostoru. Grillakis (2019) očekává nárůst extrémního půdního sucha bez ohledu na vývoj předpokládaných emisních scénářů.

Výsledky ukázaly, že biochar produkovaný při teplotách 450 a 550 °C podporuje tvorbu organo-minerálních komplexů a zlepšuje strukturu. Zároveň má největší specifický povrch. Celkově byla jako nejúčinnější vyhodnocena teplota 550 °C. Cenný je především vliv takto vyrobeného biocharu na množství žádoucích vodostálých makroagregátů, zvýšení pórovitosti a obsah dostupné vody v půdě.

Změny chemických a povrchových charakteristik biocharu jsou tedy přímo závislé na teplotě pyrolýzy, a proto by nalezení ideální teploty bylo velkým přínosem pro půdy obohacené tímto materiálem. Závěry této studie však není možno generalizovat. Vždy je třeba brát v úvahu charakteristiky pyrolyzovaného materiálu, jelikož z každé vstupní suroviny vznikne biochar s konkrétními specifickými vlastnostmi.

Stejně důležitým faktem je také velmi odlišná odpověď různých půd na aplikaci biocharu. Výsledky, které byly dosaženy v půdách jílovitých, nemusí zdaleka odpovídat potenciálním výsledkům dosažených například v půdách písčitých apod.

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The Impact of Pyrolysis Temperature on Biochar Properties and Its Effects on Soil Hydrological Properties

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Abstract: Soil structure is a crucial constituent influencing soil organic richness, rooting systems, and soil moisture conservation. Adding biochar to the soil, which directly affects aggregation, can significantly alter the soil moisture status. The extent of this impact is influenced by the temperature at which pyrolysis biochar is formed. The impact of biochar derived from wheat straw made at 350, 450, 550, and 650 °C (B_{350}, B_{450}, B_{550}, B_{650}) on soil aggregation and moisture retention was evaluated in this study. Based on the results, B_{550} had the largest mean weight diameter, most water-stable aggregates, and highest available water content compared to the control, with increases of 235%, 39% and 166% compared to the control. On the other hand, B_{350} was identified as the weakest treatment, with no significant difference from the control. Using B_{550} and B_{650} significantly reduced the soil bulk density by 13% and 12% compared to the control. Therefore, the formation of micro-aggregates, the development of soil porosity, and the subsequent increase in soil available water are unavoidable during the addition of B_{550}. The change in the hydrophilic character of biochar and the attainment of an optimal oxygen/carbon ratio with pyrolysis degradations is a critical factor in soil hydrology issues.

Keywords: bulk density; clay particle; organic carbon; porosity; soil moisture

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1. Introduction

Soil is a diverse natural ecosystem made up of minerals, organic matter, gases, liquids, and organisms that interact in a variety of ways [1]. The majority of terrestrial plants rely on soil for both quality and quantity, and hence healthy soil is crucial [2,3]. Many concepts deal with soil fertility, quality, and security [4]. For example, the "One Health" concept links human, animal and environmental health [5]. Lehmann et al. [6] pointed out that the designation of soil quality and soil health should not be confused. Soil quality is mainly related to ecosystem services concerning people. A lot of authors have already investigated ecosystem services, and this issue is relatively well described [1–3,7]. However, soil health goes beyond human health to broader sustainability goals, including the planet's health. Farming management must aim to support biological diversity, water quality, suitable climate, recreation, and human and planetary health [6]. According to Nannipieri et al. [8], healthy soils must fulfil many ecosystem services, including maintaining plant and animal productivity and biodiversity, maintaining or improving water and air quality, and promoting human health.

Severe hydrological extremes, such as long-term drought and extreme precipitation, have risen as a result of climate change [9]. This might cause an increase in global crop production instability [10]. Optimizing soil water content could encourage agroecosystems and soil microbial populations that rely on water to be more flexible [11]. Using ecological and pragmatic approaches to improve soil fertility is essential [12,13]. Biochar has been recognized as a solution to the problematic soils [14]. This carbonaceous material produced by pyrolysis of biomass waste presents a profitable and effective strategy to increase soil fertility and simultaneously sequester soil carbon [15,16].

Biochar as a soil amendment can increase soil water availability [17], water holding capacity [18], soil aeration [19]. Feedstock, pyrolysis circumstance, and soil characteristics all influence these features. Among these parameters, pyrolysis temperature has the greatest influence on the final biochar product [20].

The surface area characteristics and mineral proportion of biochar are all affected by the pyrolysis temperature [21–23]. Regardless of the feedstock used, the formation of microstructure and an increase in the surface area of biochar has frequently been documented with increasing pyrolysis temperature [24–26]. An opening of the internal structure of willow biochar was observed when the pyrolysis temperature was ≥ 450 °C [27]. Some studies also reported that biochars produced in slow pyrolysis improved available water content (AWC) in both fine- and course-textured soils [28–30]. In practice, AWC is the most essential factor in irrigation schemes; for example, with a greater AWC, the interval of watering and the volume of irrigation water used may be minimized. The use of biochar has a positive impact on the moisture content of the soil [31,32]. Even when increasing the pyrolysis temperature to 600 and 800 °C, the total pore volume and phosphate absorption rate of biochar were shown to decrease [33]. The suggested mechanisms for this are the blockage and collapse of the pore structures by melting of the material during pyrolysis [34]. However, in three agricultural soils, biochars produced from straw and wood at varying temperatures had no beneficial impact on available water [35].

On the other hand, there are some factors that are directly affected by biochar amendment, and which play important roles in altering the water capacity in the soil, such as a decrease in the soil bulk density [36], an increase the total soil pore volume and alteration of the pore-size distribution [37], the expansion of the soil surface area, particularly in sandy clay soil [38], and the expansion of soil aggregation [39]. However, many of these proposed mechanisms have not been validated on the basis of direct evidence. Nevertheless, the role of soil aggregates in water retention cannot be ignored they affect the soil water retention through the pore structure. The capacity of a soil to store and fix organic carbon (OC) is strongly affected by aggregate stability [40]. Soil aggregate distribution is an important characteristic of soil structure that regulates soil moisture. Aggregates of different sizes have different effects on diffusion of gases, water, nutrients, and dissolved OC [41], and also on germination of seeds and plant growth. For instance, a fine seedbed with aggregates of less than 5 mm is good for crop establishment [42], while a soil with aggregates of 5 mm size is advantageous for plant growth [43]. A rougher aggregate structure could promote evaporation [44], decrease ion exchange activities [45], and reduce oxygen level in the inner portion of the aggregates owing to bioactivities [46]. Sustained aggregates demand a higher volume of linked pores in topsoil [31], which have the ability to speed up water ingress [32].

Various studies have looked into changes in soil structure and the effect of aggregation in water retention capacity. On the other hand, it appears that the use of biochar in the soil has a direct impact on the aggregation process due to its surface qualities. As a consequence, biochar-treated soils are considered to have a greater moisture potential than soils without biochar. It has been demonstrated that the feedstock and pyrolysis conditions have a significant impact on how effective biochar is in soil. To the best of our knowledge, the literature has not sufficiently investigated how the temperature of pyrolysis affects soil aggregation and moisture. Therefore, the focus of this research was on observing how changing pyrolysis temperature affected the moisture qualities of soil in terms of soil aggregation indices with a closer look into produced biochar structure. Furthermore, determining the proper pyrolysis conditions with which to achieve the best efficiency of wheat biochar with respect to water retention characteristics was an alternative objective.

2. Materials and Methods

2.1. Experimental Design

This study's soil came from a research location at the Faculty of Agriculture, University of Guilan in Rasht, Iran (37°11′59.3″ N 49°38′54.6″ E). The soil has a clay texture (clay: 53%, silt: 29%, sand: 18%) and it is classified as Typic Hapludalfs. Biochars (B) derived from wheat straw were carbonized during 2 h at four pyrolysis temperatures (350, 450, 550, and 650 °C) in an electrical laboratory furnace equipped with a temperature controller with limited air access and the speed of the furnace heating was 10 °C min^{-1}. After spending 1 day cooling down, the biochars were ground to a size smaller than 1 mm, following which they were ready to be added to the soil. Therefore, following treatments were used: C (control without biochar), B_{350}, B_{450}, B_{550}, and B_{650}. Three replications were performed. All treatments were applied at 3% by weight of biochar to soil and mixed well in plastic pots (21 cm width, 30 cm depth, and 3 kg soil capacity). The application rate of biochar was selected based on frequently used in conducted pot experiments [39,47,48]. The pots were then watered (field capacity plus 20%) and dried (permanent wilting point) in a controlled environment. The pots were placed in a greenhouse at 25 °C for 7 days to check the moisture level. The incubation time was 5 months. After that, two undisturbed and disturbed soil samples collected from each pot for analysis of soil physical and chemical characteristics.

2.2. Biochar Characteristics

The analyses of biochar properties are shown in Table 1. The pH was determined using a 1:20 (w/v) biochar to water ratio [49]. An elemental analyzer was used to detect total carbon, hydrogen, and nitrogen (Perkin Elmer 2400 II). The ammonium acetate technique was used to determine CEC and exchangeable cations [50]. The Brunner, Emmett, and Teller (BET) approach was used to calculate the specific surface area [51]. To look into the effects of varying the pyrolysis temperature on the microstructure of biochar more thoroughly, scanning electron microscope (SEM) was used (Hitachi-TM3030, Japan). Figure 1 shows the results of SEM with high magnificent. The functional groups in the produced biochars used in this study were analyzed using a Fourier transform infrared (FTIR) spectrophotometer in the mid-infrared region, from 4000 cm^{-1} to 400 cm^{-1}. The resulting FTIR spectra are shown in Figure 2.

Table 1. Characteristics of biochar (B) made from wheat straw at four different pyrolysis temperatures (350, 450, 550 and 650 °C).

Property	B_{350}	B_{450}	B_{550}	B_{650}
* SSA (m^2 g^{-1})	40.1 ± 2.53	51.3 ± 2.16	85.8 ± 3.18	70.4 ± 2.13
pH	7.7 ± 0.02	8.5 ± 0.03	8.9 ± 0.02	11.7 ± 0.02
CEC (cmolc kg^{-1})	15.3 ± 1.21	19.5 ± 1.56	43.4 ± 2.15	37.2 ± 2.82
C (%)	30.1 ± 1.09	42.1 ± 1.68	52.4 ± 2.24	57.6 ± 1.97
H (%)	3.56 ± 0.03	3.22 ± 0.02	2.51 ± 0.02	1.94 ± 0.01
O (%)	14.8 ± 0.92	13.6 ± 0.67	12.9 ± 0.38	12.4 ± 0.49
N (%)	1.39 ± 0.01	1.25 ± 0.01	1.64 ± 0.02	1.53 ± 0.02
O/C ratio	0.49 ± 0.01	0.32 ± 0.01	0.24 ± 0.01	0.21 ± 0.01
Biochar yield (%)	26.2 ± 1.54	37.4 ± 2.81	45.3 ± 2.93	16.8 ± 0.97

* SSA: Specific surface area; CEC: cation exchange capacity, C: carbon, H: hydrogen, O: oxygen, N: nitrogen.

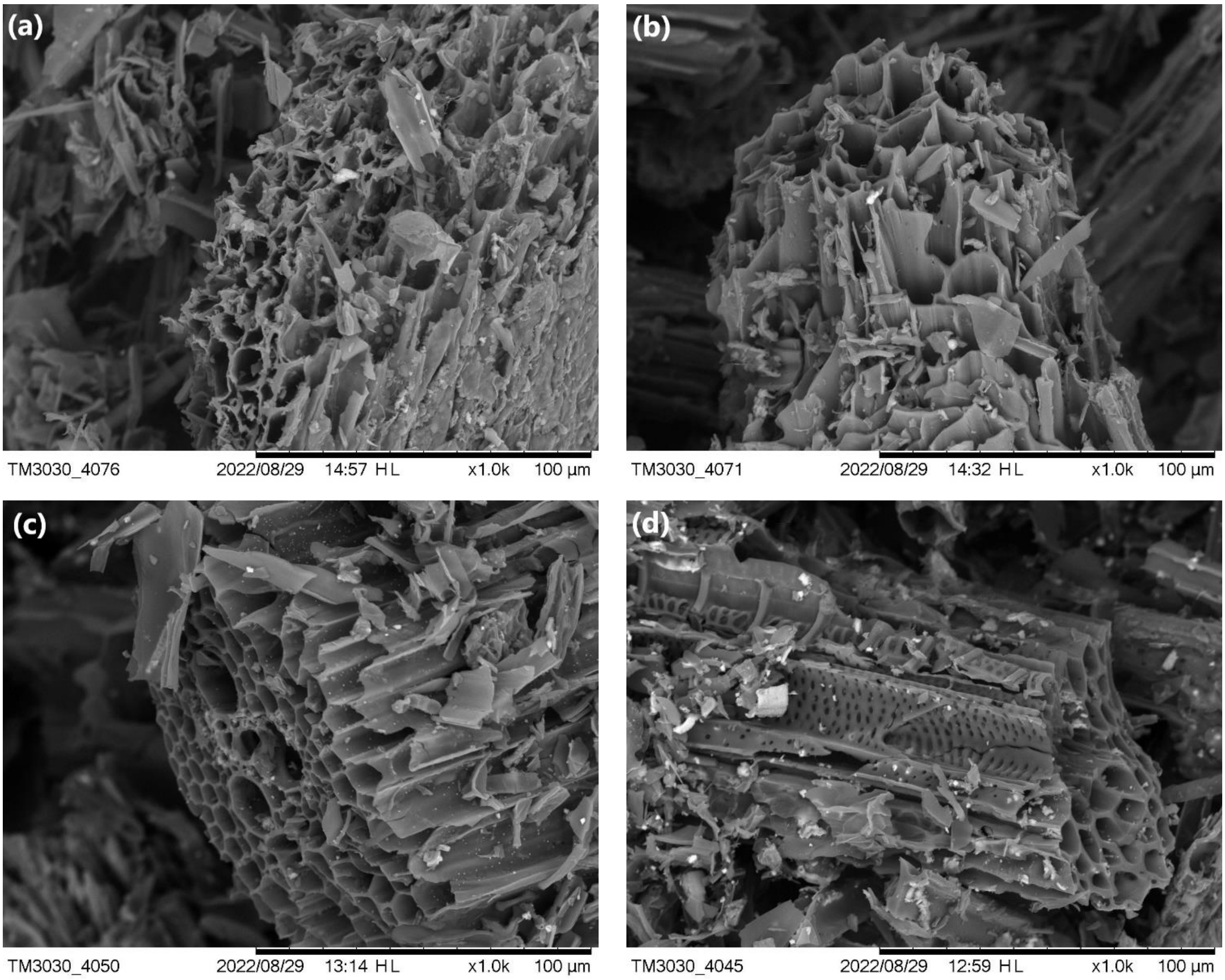

Figure 1. Scanning electron microscopy (SEM) images of biochar produced at (**a**) 350 °C, (**b**) 450 °C, (**c**) 550 °C, and (**d**) 650 °C.

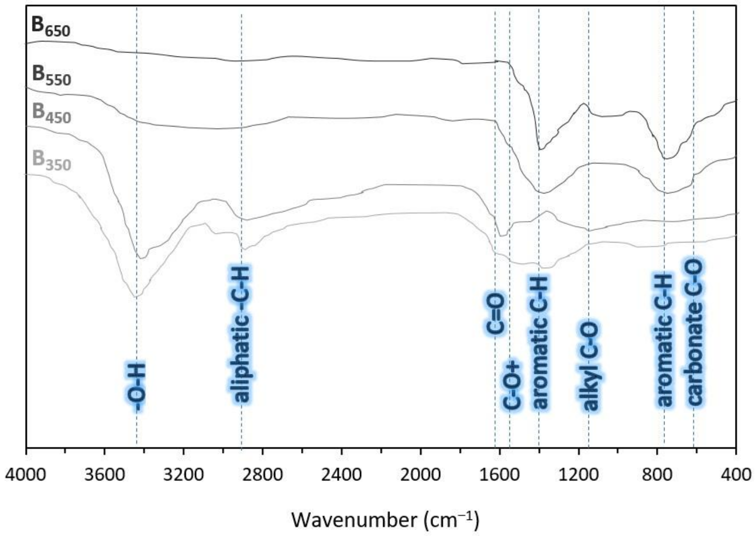

Figure 2. Fourier transform infrared (FTIR) spectra of four different biochar.

2.3. Soil Characteristics

The wet-sieving process was used to examine the wet aggregate size distribution. After open sun-drying, the soils were moistened with tap water for roughly 24 h. The soil was then soaked in a bucket of tap water and sieved at 35 oscillations per min (with a 35 mm amplitude) for 10 min on a set of sieves with apertures 2, 1, 0.5, 0.25, and 0.053 mm in diameter. After wet-shaking, the remaining material in every sieve removed carefully and dried at 105 °C. The weight ratio of aggregates from each sieve on the total weight of aggregates was computed to determine the aggregate size distribution. Using wet sieving results, the mean weight diameter (MWD) of the soil aggregates was calculated as follows [52]:

$$MWD = \sum_{i=1}^{n} \overline{Xi}\, Wi, \tag{1}$$

where $\bar{X}$ denotes the average diameter of the aggregates left on each sieve, Wi denotes the weight ratio of aggregates per sieve to the total weight of the soil, n denotes the number of sieves used.

To evaluate water-stable aggregates, 4 g of 1–2 mm air-dried aggregates were loaded into a 0.26 mm sieve, pre-wetted with water for 24 h, and then shacked 35 times min^{-1} vertically approximately 1.5 cm for 3 min using a single-sieve wet-sieving technique [52]. After drying, the weight of unstable and stable aggregates was calculated. The water-stable aggregates (WSA) index is computed as follows:

$$\text{WSA} = \frac{W_a - W_c}{W_o - W_c} \times 100, \tag{2}$$

where W_a denotes the weight of material on the sieve after wet sieving, W_c denotes the weight of sand material, W_o denotes the weight of aggregates placed on the sieve prior wet sieving.

The soil bulk density (BD) was measured by the clod method, and then the soil porosity was calculated using BD values [53]. Spectrophotometry (PerkinElmer Optima 7300V) was used to estimate the quantity of soluble base cations (Ca^{2+} and Mg^{2+}), and the flame photometer was used to calculate Na+ (M410 Sherwood). The sodium absorption ratio (SAR) was then computed using the following formula:

$$\text{SAR} = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}} \times 100, \tag{3}$$

2.4. Water Retention Capacity

Using porous plate funnels and pressure plate equipment, the soil water content curves were calculated [54]. The imposed tensions were 0, −10, −33, −100, −300, −500, and −1500 kPa which are equals to 0, 2, 2.5, 3, 3.5, 3.7, and 4.2 pF (log matric potential). The field capacity (FC) and the permanent wilting point (PWP) were determined to be −33 and −1500 kPa, respectively. Three replications were performed. The difference between FC and PWP was used to compute the available water content (AWC).

2.5. Data Analysis

One-way analysis of variance (ANOVA) was performed to examine the significance of differences in soil parameters among treatments. Lowercase letters in the figures indicate statistically significant differences after the least significant difference (LSD) test at $p < 0.05$. To analyzing existing correlation between pyrolysis temperature and soil properties, linear regression was performed as follows: a) mean of predicted values and residuals, b) normality of unstandardized residues values ($p > 0.05$) by Shapiro–Wilk test, c) the existence of potential outliers by Cook–Weisberg test, (d) the presence of autocorrelation between regression variables by Durbin–Watson test and e) the significant of regression model by Fisher–Snedecor test significance. SPSS 26.0 was used to analyze the data, and Excel 2020 was used to create all of the figures.

3. Results

3.1. Changes in Soil Characteristics

Applying B_{450}, B_{550}, and B_{650} treatments significantly affected MWD and WSA ($p < 0.05$) (Figure 3). The highest MWD and WSA were attained with B_{550}, with an increase of 235% and 39% compared to the control. The second highest values for both MWD and WSA were obtained with B_{650} with an increase of 157% and 28% compared to the control. MWD and WSA of B_{650} did not significantly differ from B_{450}, and the control and B_{350}.

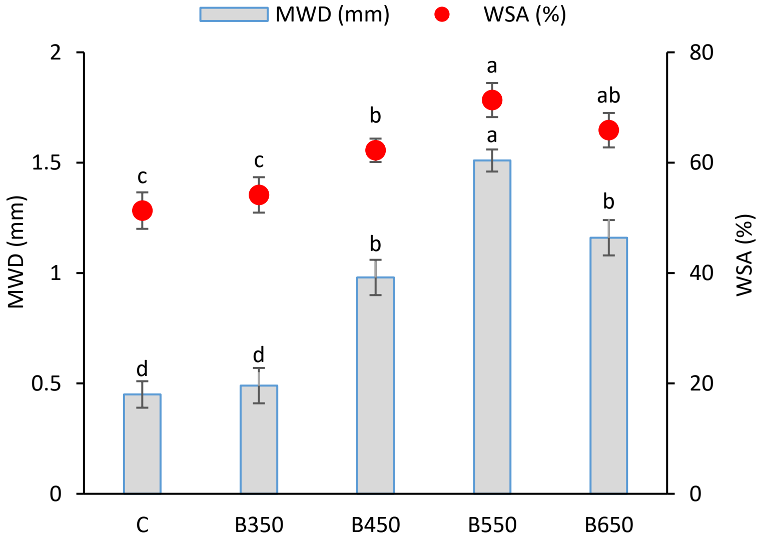

Figure 3. Effect of biochar (B) treatments on (a) mean weight diameter (MWD) and water-stable aggregates (WSA). Different lowercase letters indicate differences ($p < 0.05$). Bars represent standard errors ($n = 3$).

The quantity of micro-aggregates in the soil was affected by the biochar treatments ($p < 0.05$) (Figure 4). B_{550} significantly increased the percentage of micro-aggregates in the soil from 43% (control) to 55%. Additionally, B_{350} and B_{450} were jointly in second place, without a significant difference between them but they were significantly lower than B_{550}. Using B_{650}, on the other hand, did not result in a significant change from the control. On the other hand, the value of SAR showed a significant increase compared to the control, except for B_{550}, which did not significantly differ from the control. The highest SAR resulted from the application of B_{650}, with an increase of 129% compared to the control.

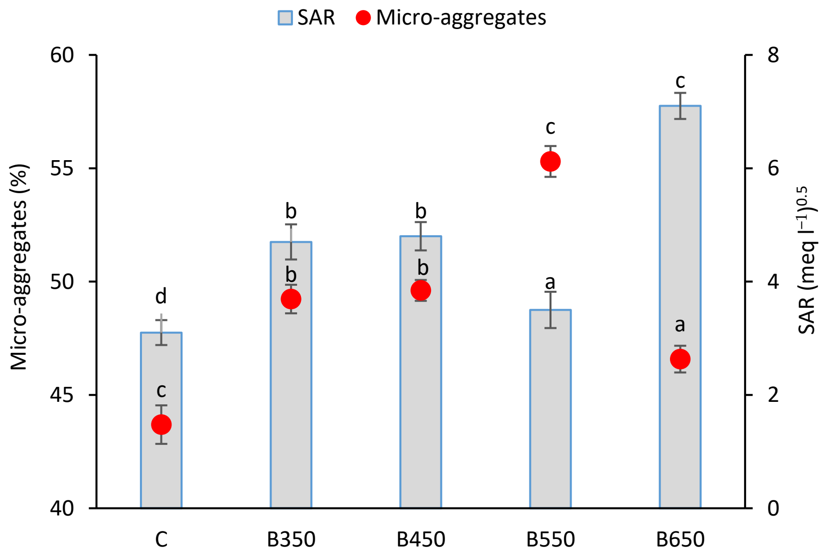

Figure 4. Effect of biochar (B) treatments on sodium absorption ratio (SAR) and percentage of micro-aggregates. Different lowercase letters indicate differences ($p < 0.05$). Bars represent standard errors ($n = 3$).

Biochar treatments had a significant impact on soil BD and porosity ($p < 0.05$) (Figure 5). Applying B_{550} and B_{650} significantly increased the porosity by 15% and 14% compared to the control, respectively, but decreased the BD by 13% and 12% compared to the control, respectively. The B_{350} treatment had the worst results, since neither the porosity nor the BD differed from the control. B_{450} showed values intermediate between the control and B_{550} and B_{650} for both parameters.

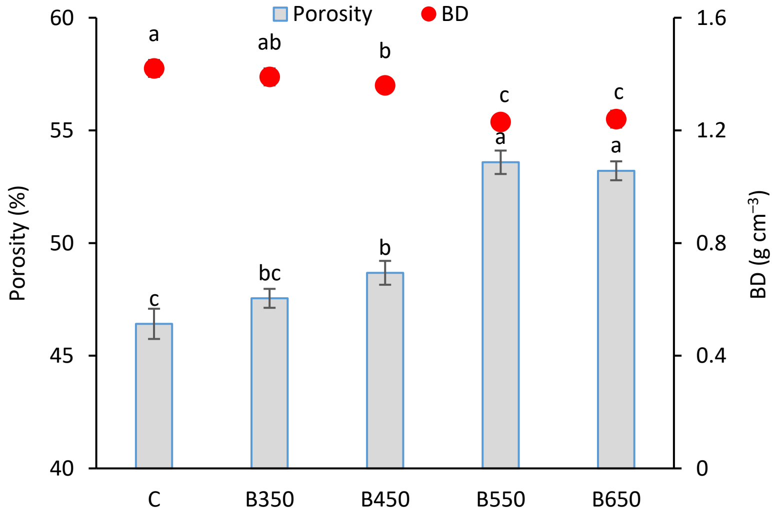

Figure 5. Effect of biochar treatments on total soil porosity and bulk density. Different lowercase letters indicate differences between the treatments ($p < 0.05$). Bars represent standard errors ($n = 3$).

3.2. Water Retention

The use of biochar had a considerable impact on FC, PWP, and AWC (Figure 6). The FC significantly increased with B_{450} and B_{550} by 14% and 17% compared to the control, respectively. Meanwhile, the FC with B_{350} and B_{650} as lower compared to B_{450} and B_{550} and did not differ compared to the control ($p < 0.05$). The three treatments B_{450}, B_{550} and B_{650} significantly decreased the PWP by 20%, 23% and 21% compared to the control, respectively. There was no noticeable difference between B_{350} and the control. The highest AWC was attained when applying B_{450} and B_{550} with an increase in 146% and 166% compared to the control, respectively. Additionally, B_{650} increased the AWC by 89% compared to the control. The control and B_{350}, on the other hand, showed no significant difference.

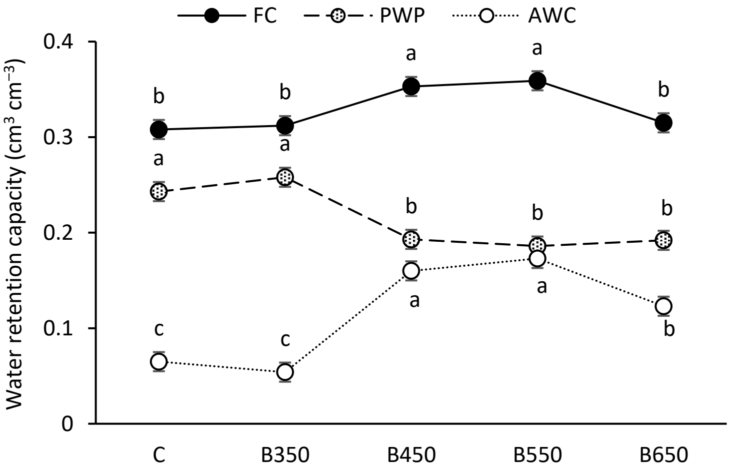

Figure 6. Effect of biochar treatments on field capacity (FC), permanent wilting point (PWP) and available water content (AWC). Different lowercase letters indicate differences between the treatments ($p < 0.05$). Bars represent standard errors ($n = 3$).

The statistical characteristics of the regressions between pyrolysis temperature and soil properties are presented in Table 2. The residuals of all models passed heteroscedasticity for the existence of potential outliers using the Cook–Weisberg test. The results of the Shapiro–Wilk test significantly showed that residuals had a normal distribution due to their having a sig. value of greater than 0.05. The Durbin–Watson statistic ranged from 0 to 4, with a value of 2.0 indicating no autocorrelation. Values close to 0 mean that there is a positive autocorrelation and values close to 4.0 indicate negative autocorrelation. In this study, autocorrelation between residuals was not observed on the basis of the Durbin–Watson test. The regression model was significant according to the Fisher–Snedecor model significance test. Because the mean of the residuals was close to zero, the residual distribution was close to a normal distribution, and therefore the model was better fitted. As can be observed from Figure 7, the results show that there is positive relationship between soil characteristics and pyrolysis temperature, such that coefficients of determined were obtained for them as follows: $R^2 = 0.61$ for MWD, $R^2 = 0.53$ for WSA, $R^2 = 0.46$ for micro-aggregates, $R^2 = 0.51$ for SAR, $R^2 = 0.53$ for porosity, and $R^2 = 0.65$ for BD.

Table 2. The statistical characteristics of the dependence variables.

Constant Variable	Dependent Variable	*n*	R	R^2	F Test (Sig.)	S-W Test (Sig.)	D-W Test	Mean of Predicted Values	Mean of Residual
* Pyrolysis temp.	MWD	12	0.78	0.61	191.9 (0.000)	0.71	1.814	10.87	0.000
Pyrolysis temp.	WSA	12	0.73	0.53	459.6 (0.000)	0.62	1.731	56.43	0.000
Pyrolysis temp.	Micro-agg	12	0.69	0.46	419.2 (0.000)	0.36	1.839	50.21	0.000
Pyrolysis temp.	SAR	12	0.71	0.51	205.8 (0.000)	0.55	1.667	6.121	0.000
Pyrolysis temp.	Porosity	12	0.73	0.53	457.4 (0.000)	0.48	1.968	54.73	0.000
Pyrolysis temp.	BD	12	0.81	0.65	116.3 (0.000)	0.79	2.109	4.986	0.000

* temp.: temperature, MWD: mean weight diameter, WSA: water stable aggregate; Micro-agg: micro-aggregate, SAR: sodium absorption ratio, BD: bulk density, *n*: observations, R: coefficient of correlation, R^2: coefficient of determination, F: Fisher–Snedecor test, S-W: Shapiro–Wilk test, and D-W: Durbin–Watson test.

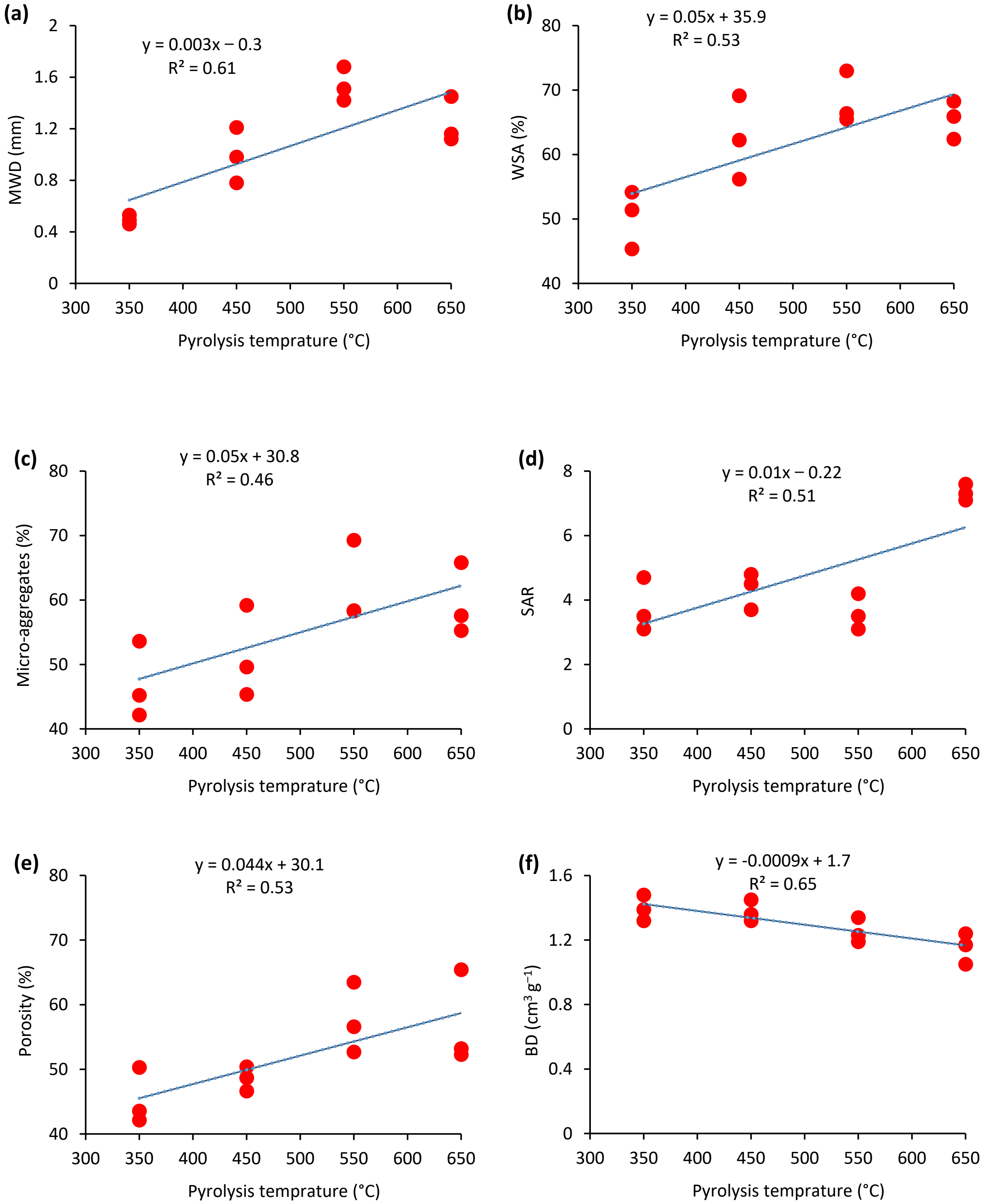

Figure 7. Regression relationships between the pyrolysis temperature of wheat biochar for (**a**) mean weight diameter (MWD), (**b**) water-stable aggregate (WSA), (**c**) micro-aggregates, (**d**) sodium absorption ratio, (**e**) porosity, and (**f**) soil bulk density (BD). The values on each graph represent the total number of treatments and replicates.

4. Discussion

In this study, adjusting the biochars' pyrolysis temperature resulted in appreciable changes in the soil's porosity and bulk density, and, consequently, its hydrological characteristics (Figure 5). These changes can be interpreted on the basis of the occurrence of several mechanisms that are interrelated. Firstly, the change in the hydrophilic nature of biochar with pyrolysis degradations is a key factor in this regard. The O/C ratio is a practical indicator for the determination of the level of the conversion of biomass to biochar, and also the rate of carbonization [55]. When the pyrolysis temperature increases, the O content falls during the decarboxylation reaction, lowering the O/C ratio [56,57]. Higher loss of O indicates higher carbonization of the feedstock, formation of more fused aromatic rings, and stronger C structure of the biochar [58]. The polarity of biochars is determined by the O/C molar ratio [22]. Nevertheless, the values of 0.2 and 0.4 as lower and upper limits of the O/C ratio, respectively, are accepted for the characterization and differentiation of biochar from soot and biomass [55]. A higher O/C ratio means less change in the feedstock and better biomass features in the carbonized product [58]. Overall, a O/C ratio between 0.2 and 0.4 means more carbon skeletons and oxygenated functional groups. As shown in Table 1, the lowest and highest O/C ratio obtained from B_{650} and B_{350}, respectively, which would be a reasonable justification for that assertion. Therefore, B_{350} having the worst performance can be explaining by there being less alteration during the pyrolysis process, and the fact that it retains its feedstock characteristics at the end of production, as B_{650}, which has a much higher loss of O, possesses characteristics outside the range of biochar and has become a soot. Raising the pyrolysis temperature to above 550 °C appears to lessen biochar polarization, making the biochar surface less hydrophilic. Moreover, it was observed that when the pyrolysis temperature rose to above 500 °C, the yield of biochar synthesis decreased by 10% for every 100 °C increase [59]. For this reason, B_{450} and B_{550} exhibit more benefits compares to the two other treatments. This means that B_{450} and B_{550} had a sufficiently porous C structure and oxygenated functional groups in their structure to provide room to contain more moisture [26]. The development of an arranged carbon skeleton with an increase in pyrolysis temperature is clearly visible from the microscopic images of the produced biochars (Figure 1). Therefore, this stable C structure can be considered an effective factor for improving soil AWC. A notable distance between FC and PWP moisture points in the water retention curve after the application biochar produced at high temperature can therefore be inferred (Figure 6). Low temperatures (< 550 °C) have been shown to produce biochars with more oxygen-containing functional groups, resulting in an amorphous C matrix that increases nutritional availability [38]. According to the FTIR test in the current study, the sharp peaks present in B350 and B450 at wavenumbers of 3430 and 1620 cm^{-1}, which can be attributed to functional hydroxyl and carboxyl groups, can support that claim (Figure 2). However, the hydrophobicity is increased as a negative property [60]. Maize stalk biochar generated at 650 °C was shown to have no effect on aggregate stability due to the lack of oxygen-containing functional groups [26]. Throughout, the best pyrolysis temperature range to generate optimal biochar with low hydrophobicity was found to be between 400 and 600 °C [21]. Additionally, because of the prevalence of non-polar aliphatic and aromatic groups in organic compounds, the relatively low pyrolysis temperature (450 °C) induces increased water repellent activity. This hydrophobic situation provides negative capillary pressure, keeping water from entering the pores [61]. Furthermore, higher temperatures resulted in a loss of hydrogen (H) owing to the increased carbonization and a loss of nitrogen (N) due to the evaporation of N-containing compounds. It has been demonstrated that at temperatures above 400 °C, a significant proportion of N is lost as N_2O, NO, and NO_2 [62]. When we increased the temperature from 350 to 650 °C in our experiment, biochar yield decreased progressively. This is most likely due to the loss of volatile organic molecules at high temperature, resulting in the formation of tiny pores, while primary organizational structures such as cellulose are preserved [59]. These tiny pores are clearly visible in the SEM image of B_{650} (Figure 1). This process created a well-developed microporous structure in the biochar and resulted in low weight, low density, and multiple micro-pores [36–38]. Gradual increase in soil porosity, as well as the decrease in bulk density with increasing pyrolysis temperature, demonstrate the effectiveness of changes in weight and volume of biochars.

This is confirmed by the fact that porosity has a positive connection with pyrolysis temperature and BD has a negative relation with pyrolysis temperature.

The second important factor that plays a key role in improving the water content in soil is the interface between biochar particles and soil aggregation [25], as the positive correlation of MWD and WSA versus pyrolysis temperature confirms (Figure 7). The distribution of micro-aggregates (<250 μm) in soil is a key feature of soil structure, and it is considered to influence soil water retention [63]. These micro-aggregates are made up of a variety of mineral, organic, and biotic components that are linked together with biochemical functions throughout soil formation. Stable micro-aggregates have the capability of increasing flux and impacting unsaturated water conductivity by providing a higher number of linked pores [11,26]. MWD and WSA significantly changed with different pyrolysis conditions, with B_{550} showing the highest values for both parameters (Figure 3). This can be attributed to the proper pyrolysis conditions exhibited by B_{550}, and thus the higher organo-mineral component in the soil. The most critical parameters for improving AWC were features such as specific surface area and adequate soil OC [29]. It has been proven that increasing pyrolysis temperature to values higher than 550 °C, regardless of the type and rate of feedstock, significantly decreases the OC, basal soil respiration, and, consequently, aggregate stability indices [63]. Therefore, the biggest increase in micro-aggregates being recorded for B_{550} could be related to the greater OC value in the B_{550}. This is important, because biochar providing OC and linking to the soil particles results in the formation of stable organo-minerals that are less vulnerable to degradation. According to certain studies, a considerable proportion of OC in biochar generated above 650 °C is recalcitrant OC, but the proportion of recalcitrant and labile OC in biochar produced at temperatures below 550 °C is about equal [30,63]. Therefore, the presence of more labile OC using biochar in the soil indicates the improvement of aggregation due to the creation of organo-mineral bridges between soil particles. This is supported by the positive correlation between micro-aggregates and pyrolysis temperature. Additionally, the lower percentage of micro-aggregates in B_{650} than B_{550} is related to their alkaline characteristics. B_{650} has much higher pH compared to the other treatments (Table 1), which indicates an increase in the percentages of alkaline cations (e.g., Na^+, K^+, Ca^{2+}, and Mg^{2+}) [26,64,65]. In addition, the increased sodium adsorption ratio (SAR) in B_{650} indicates that significant Na^+ has been added to the soil (Figure 4). As a consequence, when Na^+ is available in exchangeable form in the soil, it substitutes Ca^{2+} and Mg^{2+} adsorbed on the soil clays, causing soil particle distribution. Since the flocculation of clay particles is one of the basic conditions for the formation of micro-aggregates, this dispersion results in breakdown of soil micro-aggregates. For this reason, a decrease in micro-aggregates occurred with increasing SAR could be observed in B_{650}. This argument is backed up by the fact that SAR and pyrolysis temperature have a positive relationship. Figure 8 summarizes the percentage of changes in soil characteristics affected by different pyrolysis temperatures in this study.

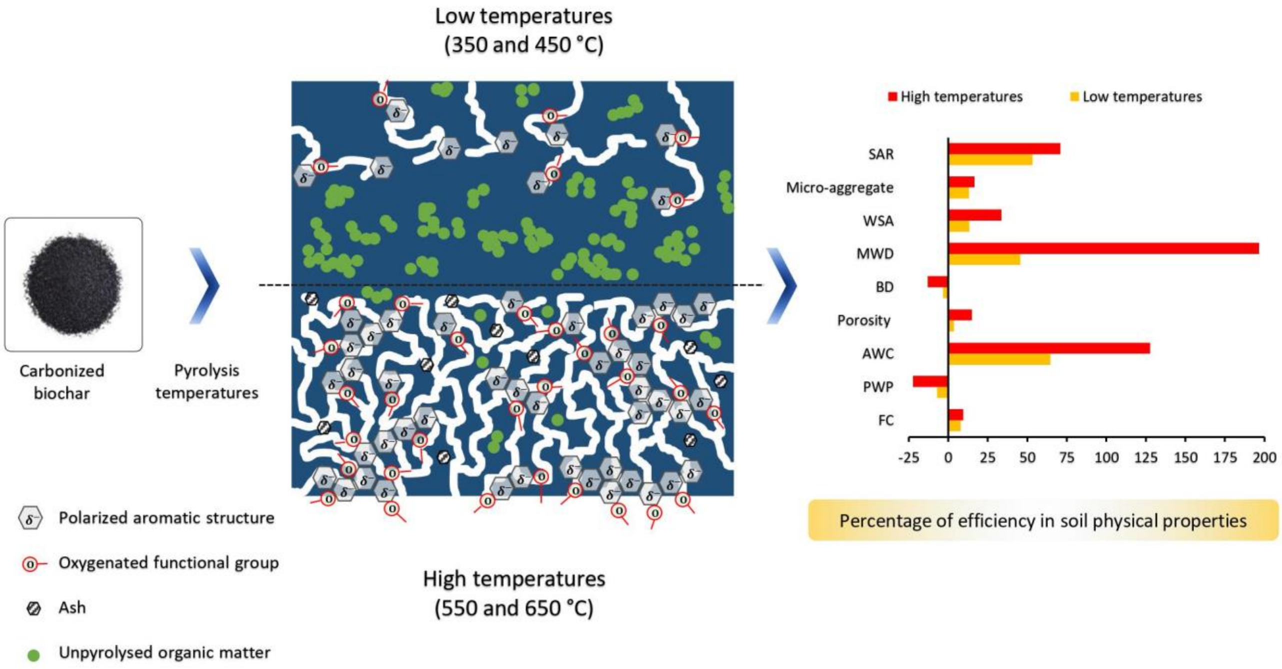

Figure 8. Summary of changes in soil characteristics affected by different pyrolysis temperature.

5. Conclusions

To investigate the impact of biochar on aggregate function in terms of boosting soil moisture capacity, an experiment was performed in which four wheat biochar samples that had been pyrolyzed at various temperatures were compared. The results showed that increasing pyrolysis temperature to more than 550 °C notably boosted the hydrophobicity in biochar structure due to the much higher loss of O content. Additionally, biochar produced at a temperature of 450 to 550 °C boosted organo–mineral complexes and improved the soil structure due to its possessing a robust carbon skeleton, increased specific surface area, and more cations ready to bind to soil particles. Overall, B_{550} was recognized as being the most efficient treatment, which has an obvious impact on soil mean weight diameter, water stable aggregate, porosity, and soil available water content, which exhibited 235%, 39%, 15% and 166% increases, respectively, compared to the control. Therefore, changes in the chemical and surface characteristics of biochar are seen as a function of temperature, and therefore understanding the ideal temperature will have a big influence on the structure of soil modified with biochar. The importance of this issue becomes clearer when the physiological differences between different feedstocks are considered, such as resistance and degradability at pyrolysis temperatures. Therefore, in order to improve biochar efficiency with respect to soil hydrological concerns, the appropriate temperature for various feedstocks must be determined based on the region's agricultural waste management strategy.

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Publikace 5: Metaanalýza dopadů různých oxidačních metod na povrchové vlastnosti biocharu

Ghorbani, M., Konvalina, P., Kopecký, M., & Kolář, L. (2022). A meta-analysis on the impacts of different oxidation methods on the surface area properties of biochar. Land Degradation & Development. 1–14. DOI: 10.1002/ldr.4464.

Bylo publikováno obrovské množství prací o pozitivním vlivu biocharu na zemědělskou půdu. Řada z nich se zabývá tím, jak benefity biocharu maximalizovat. Jednou z cest je oxidace povrchu biocharu. Bylo například zjištěno, že oxidace zlepšuje povrchové vlastnosti, jako je zvýšení kationtové výměnné kapacity nebo množství funkčních skupin obsahujících kyslík. Závěry studií zkoumajících oxidaci biocharu se však mnohdy rozcházejí.

Z tohoto důvodu byla provedena meta-analýza (64 článků) zkoumající účinky různých oxidačních metod (kyselé, alkalické, oxidy kovů, fyzikální a přírodní oxidace) a některých dalších faktorů (doba modifikace, teplota pyrolýzy, typ suroviny) na kationtovou výměnnou kapacitu, obsah mikropórů, povrchovou plochu a funkční skupiny obsahující kyslík u různých druhů biocharů.

Metaanalýza odhalila, které technologie oxidace biocharu se zdají být nejslibnější. Vyhodnocená data ukázala, že kyselá postpyrolytická oxidace dosáhla největšího zlepšení v parametrech kationtové výměny, zvětšení povrchu a nárůstu funkčních skupin obsahujících kyslík. Vlastnosti modifikovaného biocharu jsou ovlivněny teplotou pyrolýzy a typem vstupních surovin. Za nejúčinnější pyrolýzní teplotu je považována 400–550 °C. Zvýšení teploty pyrolýzy nad 550 °C má již negativní vliv na výskyt funkčních skupin, a tedy i sorpční charakteristiky biocharu. Co se týče vstupních surovin, nejlepší výsledky byly zjištěny u materiálů, jako je sláma, plevy, skořápky a podobná zemědělská biomasa. Při hodnocení pórovitosti bylo zjištěno, že pro její nárůst jsou třeba stejné podmínky výroby a úpravy biocharu jaké byly nejlepší pro zvýšení kationtové výměnné kapacity, funkčních skupin a plochy povrchu.

Abstract

Biochar has a beneficial impact on agricultural prosperity, according to numerous studies, and the key dispute presently is how to maximize that impact. Biochar oxidation is well-known as one of the accepted methods for increasing biochar efficiency. However, due to contradictory data presented in studies and because biochar is derived from diverse oxidation procedures, as well as, the lack of an analytical comparison between different methods, oxidation data sets require a thorough assessment that can be covered by meta-analysis. In this study, the effects of the five most common oxidation methods in the literature, namely oxidation by acids, alkaline, metal oxides, physical, and natural oxidation, on the cation exchange capacity (CEC), micro-pores (MP), specific surface area (SSA), and oxygen-content functional groups (OFGs) of biochar, were meta-analyzed. When pyrolysis conditions varied, the efficiency of various operations was also addressed. The most efficient method was acidic oxidation, which increased CEC, SSA, MP, and OFGs by 46%, 43%, 55%, and 72%, respectively. Additionally, increasing the pyrolysis temperature above 550°C is critical for lowering OFGs, which has an impact on biochar sorption characteristics. According to the findings, biochar oxidation (post-pyrolysis) is important since it creates more oxide ions on the surface area than feedstock oxidation (pre-pyrolysis). Due to their high inorganic nutrient content, crop residues such as rice husk, maize stalk, and rapeseed stem, which were classed in the intermediate group in this study, are promising feedstocks for synthesizing biochars with high SSA, MP, and CEC. Overall, when compared to other approaches, the acidic process significantly improves the surface properties of biochar.

KEYWORDS: absorbance, activation analysis, cation exchange capacity, feedstock, pyrolysis condition

Publikace 6: Srovnání účinků aplikace biocharu a kompostu na vododržnost a výnos rýže při vodním stresu: dvouletá polní studie

Ghorbani, M., Neugschwandtner, R. W., Konvalina, P., Asadi, H., Kopecký, M., & Amirahmadi, E. (2023). Comparative effects of biochar and compost applications on water holding capacity and crop yield of rice under evaporation stress: a two-years field study. Paddy and Water Environment, 1–12. DOI: 10.1007/s10333-022-00912-8.

Z hlediska lidské potravy je rýže nejdůležitější plodinou. Podílí se na zajištění energetických potřeb lidstva z 19 % (Livsey et al., 2019). Její pěstování je však extrémně náročné na vodu. Globálně je přibližně 70 % spotřeby sladké vody využíváno právě v zemědělské produkci (Campbell et al., 2017) a pěstování rýže spotřebuje více než polovinu z ní (Hang et al., 2022). Pokud nemá rýže v počátečních fázích růstu k dispozici dostatečné množství vody, ať už záplavové, srážkové či závlahové, čelí rostliny vážným vývojovým problémům (Acharjee et al., 2017).

Nedostatek vody lze kompenzovat vhodnou úpravou půdy (Erana et al. 2019). V literatuře existuje mnoho zpráv o pozitivním vlivu kompostu a biocharu na hydrologické vlastnosti půd. Jejich vzájemné srovnání za stejných podmínek však zůstalo stranou zájmu výzkumu. Tento článek se tedy zabývá použitím a vyhodnocením přínosů těchto dvou materiálů v systémech pěstování rýže s ohledem na hydrologické vlastnosti půd. Cílem studie tedy bylo srovnání účinků biocharu a kompostu přidaných do půdy na dostupnost vody a výnosnost rýže.

Studie byla provedena v letech 2020 a 2021 v Iránu. Biochar byl vyroben z rýžových slupek při teplotě 450±50 °C, kompost byl kombinací řas Anabaena azollae a dalších organických materiálů, jako je rýže a pšeničná sláma. Tyto organické látky byly zapraveny do půdy týden před výsadbou (dávka 20 $t \cdot ha^{-1}$). Pokusy běžely ve třech režimech zavlažování.

Ačkoli oba použité materiály zvyšují dostupnost živin pro rostliny a mohou být považovány za zúrodňující, byly mezi jejich účinky nalezeny značné rozdíly. Oproti biocharu má kompost nevýhody, mezi které patří menší specifická plocha povrchu, a tedy i menší schopnost vytvářet organo-minerální komplexy. Naopak biochar agregaci půdy zvyšuje. Díky tomu zlepšuje i vododržnost. Význam biocharu a kompostu, i rozdíly mezi nimi, se projevily především při horších hydrologických podmínkách. Vzhledem k tomu, že druh suroviny a nastavení procesu pyrolýzy přímo ovlivňuje fyzikální a chemické vlastnosti biocharu, mělo by být dále předmětem výzkumu, jak různé biochary ovlivňují zadržování vody v půdě.

ABSTRACT

Adding organic amendments to paddies to improve water use efciency (WUE) could be a potential strategy to improve soil water storage. This research looked at the efects of biochar and compost additions at 20 t ha−1 rates in a rice feld for two years, using three irrigation regimes called I100, I75, and I50 which indicate irrigation rates of 100%, 75%, and 50% of evaporation from class A evaporation pan. Changes in soil matric potential curves, as well as rice yield components such as height, grain yield, panicle density, and spikelets per panicle, as well as well water consumption, were measured. Adding biochar to all irrigation regimes resulted in the greatest increase in matric potential points. Biochar enhanced water holding capacity under higher evaporation stress than compost. Biochar treatment under the I50 regime increased grain yield by 35% and 30% in two consecutive years. While in compost-treated soil and I50 regime, the amount of grain yield signifcantly decreased by 7% and 38% compared to control, respectively, in 2020 and 2021. Using biochar signifcantly increased WUE in order to decrease irrigation regimes. The two years did not signifcantly difer from one another. However, using compost, WUE showed a declining trend in response to lower irrigation regimes. When evaporation is excessive and irrigation is insufcient, biochar's higher porosity and surface area, as well as its greater stability to decomposition relative to compost, may improve WUE in rice.

Keywords: Irrigation regimes · Soil moisture · Plant uptake · Water consumption

Publikace 7: Srovnání vlivu biocharu a zeolitu na půdní hydrologické indexy a růstové charakteristiky rýže

Ghorbani, M., Amirahmadi, E., Konvalina, P., Moudrý, J., Bárta, J., Kopecký, M., ... & Bucur, R. D. (2022). Comparative Influence of Biochar and Zeolite on Soil Hydrological Indices and Growth Characteristics of Corn (Zea mays L.). Water, 14(21), 3506. DOI: 10.3390/w14213506.

Hydrologickým charakteristikám půd po aplikaci biocharu se věnuje i tento článek. Studován byl zejména obsah půdní vlhkosti a vývoj rostlin kukuřice v závislosti na ošetření. Tentokrát byl biochar (z rýžové slámy, teplota pyrolýzy 500 °C) srovnáván se zeolitem, který se řadí mezi krystalické hlinitokřemičitany (Mortazavi et al., 2021) a je taktéž považován za vhodnou látku zlepšující hydrologické charakteristiky půd (Szatanik-Kloc et al., 2021). Jako modelová plodina byla vybrána kukuřice setá. Nádobový experiment byl uskutečněn v roce 2020 v Iránu s hlinitopísčitou půdou. Zkoumány byly dvě aplikační dávky (5 a 10 $t \cdot ha^{-1}$).

Výsledky ukázaly, že po přidání biocharu do hlinitopísčité půdy bylo dosaženo lepších výsledků v důsledku příznivých vlastností biocharu – vysoký specifický povrch, vysoká iontovýměnná kapacita, přítomnost funkčních skupin na povrchu biocharu. Biochar, díky svému pozitivnímu vlivu na půdní strukturu, pomohl vytvořit ideální podmínky pro tvorbu a vývoj kořenů a růst rostlin.

Překvapivým zjištěním byl negativní vliv vyšší dávky zeolitu na půdní strukturu (nejen oproti biocharu, ale i kontrolní variantě). Pravděpodobně v důsledku své hrubosti působil zeolit na rozpad půdních agregátů, čímž zvyšoval ztráty vody a v důsledku toho byl sledován negativní dopad také na vývoj rostlin.

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Comparative Influence of Biochar and Zeolite on Soil Hydrological Indices and Growth Characteristics of Corn (*Zea mays* L.)

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Abstract: Biochar and zeolite, due to their porous structure, are supposed to be appropriate soil amendments especially in agricultural areas with a lack of water or unsuitable soils with coarse texture. Two soil additions that are intended to assist an increase soil water content (AWC) are biochar and zeolite. With this aim, the effects of biochar and zeolite at two levels of 5 and 10 t ha^{-1} (known as B5, B10, Z5, and Z10) on soil hydrological properties and consequently corn growth were investigated in this study. The results showed that the application of B5 and B10 significantly improved AWC by 76% and 48% due to increasing soil micro- and meso-pores. The application of Z5 and Z10, associated with an increase of macro-pores in soil, enhanced saturated hydraulic conductivity (Ks) up to 174% and 303% and caused losses. The highest specific surface area and mean weight diameter in soil obtained from B10 had an increase of 171% and 197% over the control. Biochar treatments considerably affected plant growth features and shoot nutrient content, whilst zeolite treatments had an impact that is much less apparent than that of biochar. Observations indicate that biochar greatly boosted nutrient availability and water retention in the soil by raising the share of micro- and mezzo-pores, respectively, and as a result, has benefited plant growth. Increasing the level of biochar application from 5 to 10% would have more positive effects on the water available in the soil and on plant root systems. In contrast, the high rate of application of zeolite particles due to coarseness and adding Na^+ ions to the soil caused the dispersion of soil particles, the destruction of soil structure, increasing Ks and water loss and consequently a reduction in plant growth.

Keywords: water availability; field capacity; soil structure; porosity; soil amendment

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1. Introduction

The soil's structure, which is its most important factor, is primarily responsible for the soil's ability to provide moisture, nutrients, aeration, a habitat for microorganisms, and a suitable environment for the growth of plant roots [1–5]. Porosity, bulk density, pore size distribution, hydraulic conductivity, and ultimately the amount of water accessible for plant roots are all dramatically altered by changes in soil structure, which is defined as a change in the arrangement of organic and inorganic particles [6,7]. However, extreme hydrological events including prolonged droughts, extraordinarily high precipitation, and frequent wet–dry cycles have risen due to global climate change [8]. As a result, there may be more uncertainty over global agricultural production. Increasing the soil's ability to retain water can boost the resilience of agroecosystems and the water-dependent soil microbial ecosystems [9]. Today, it is advised to apply amendments to alter the soil structure in order to address the numerous issues related to water resources in agriculture and boost the productivity of low water soils [10–12]. Due to their porous nature, zeolite and biochar are two examples of amendment materials that appear to have the capacity to alter soil moisture conditions [13–16].

Zeolites are classified as crystalline aluminosilicates and play a significant role in soil amendments by enhancing soil aeration, nutrient availability, and plant production [17]. Along with the more than 60 known naturally occurring zeolites, the International Zeolite Association has certified more than 230 distinct zeolites and zeotype frameworks [18]. Zeolites are a common substance that can be used as a low-cost modification to reduce heavy metal toxicity [19,20]. Clinoptilolite is one of the most significant natural zeolites and is also extremely common [21]. Zeolites have an open three-dimensional structure that allows them to store water and improve nutrient availability for plants [22,23]. Additionally, zeolites have a high cation exchange capacity (CEC) [13,24]. Due to its high ion-exchange capacity and porous structure, natural zeolite is suggested for removing or stabilizing heavy metals from soil that has been anthropogenically contaminated with Cd, Zn, Pb, and Ni [25]. Due to its porous nature, zeolite has been shown in several studies to have good impacts on minimizing nitrate leaching and promoting crop development [26,27]. According to reports, the use of zeolite can increase the nutrients and water availability for plant roots due to its contribution to soil aggregation and boosting soil CEC [28,29].

Biochar, a stable carbon compound produced by the pyrolysis process, because of its potential as an agricultural soil stabilizer, has received particular attention in a number of studies on plant nutrition [30,31]. The inherent qualities of biochar, such as its high specific surface area, high porosity, and accessibility to nutrients, which make it a priceless and multifaceted soil modifier, enable the management of agricultural residues, the enhancement of the physicochemical characteristics of soil, the reduction of air, soil, and groundwater pollution, and the enhancement of plant growth [32]. The use of biochar can improve the arrangement of soil particles, as well as the physical and chemical properties of the soil, such as noticeably decreasing soil bulk density [33], increasing soil porosity to aid in plant growth and development [34], and encouraging crop nutrient uptake to boost crop yield [31]. It has been shown that biochar may greatly increase the water conductivity and field water retention capacity of farmed soils [35]. Additionally, biochar can raise soil pH, especially in acidic soils [36], as well as nutrient absorption and cation exchange capacity sorption characteristics [37]. Base cations found in biochar can form cationic bridges with clay and organic particles to combine them, improving the soil's structural conditions [38]. Numerous studies have also claimed that biochar produced through slow pyrolysis increases the amount of water that is readily available (AWC) in soils with both fine and course textures [39–42]. AWC is actually the most critical aspect in irrigation schemes; for instance, with a higher AWC, the amount of irrigation water used and the watering interval may be lowered. The moisture level of the soil was improved by the use of biochar [39,40].

Agroecosystems and water-dependent soil microbial communities may become more adaptable as a result of optimizing soil water content [43,44]. It is crucial to use practical and ecological methods to increase soil fertility. Despite several studies on the impact of zeolite and biochar on the physical and chemical characteristics of soil, there has not yet been a comparison of these two amendments. The most apparent similarity between these two amendments is that they both have porous structures. However, despite the significance of this issue in conserving soil moisture, a thorough examination of each one's impact on soil hydraulic indices has gone unreported. On the other hand, since plant growth has previously gone unnoticed, it is the simplest approach to assess each one's effectiveness. This study was carried out to compare the effects of zeolite and biochar on soil physical characteristics, particularly moisture content and corn plant development efficiency in response to soils treated with these amendments.

2. Materials and Methods

2.1. Experimental Procedure

The pot experiment was carried out in a greenhouse at the Faculty of Agriculture, University of Guilan in Rasht, Iran (37°11′59.3″ N 49°38′54.6″ E) from the beginning of June to the end of August 2020. Throughout the trial, the average day and nighttime temperatures were 23.6 °C and 15.7 °C, respectively. Relative humidity was 75% on average. The treatments were created in a completely randomized form with three duplicates. The *Zea mays* L. (corn) cultivar Single Cross 704 was the target plant for the analysis of changes in growth traits. Unbroken grains of the same size and color were cleaned in distilled water, sterilized for approximately 15 min in a solution of sodium hypochlorite at a 10% concentration, and then dried by air. After that, the grains were seeded in 6-kg plastic pots. The type of soil that was used was sandy loam. In each pot, 5 grains were sowed at a depth of 30 mm. N, P, and K were applied at levels of 480 kg N ha^{-1} (1.15 g N/pot, in the form of urea), 39.6 kg P ha^{-1} (0.126 g P/pot, in the form of calcium superphosphate), and 99.6 kg K ha^{-1} (0.313 g K/pot, in the form of potassium chloride), respectively, as base fertilizers. Zeolite and biochar were used as treatments, and they were applied at two different amounts of 5 and 10 t ha^{-1}, or 12.1 and 24.2 g/pot, respectively. The following treatments were used: Control (no zeolite or biochar), B5, B10, Z5, and Z10. The treatments and soils were uniformly combined three days prior to planting.

By pyrolyzing rice straw at 500 °C in a muffle furnace, biochar is created. Under the brand name Anzymite, zeolite was supplied by the Afrand Tosca Company. In Table 1, some characteristics of soil, biochar, and zeolite are listed.

Table 1. Chemical characteristics of soil and applied materials.

	pH	**CEC ($cmol^{(+)}$ kg^{-1})**	**OC (%)**	**Ca^{2+} ($cmol^{(+)}$ kg^{-1})**	**Mg^{2+} ($cmol^{(+)}$ kg^{-1})**	**Na^{+} ($cmol^{(+)}$ kg^{-1})**	**Available P (mg kg^{-1})**	**Available K (mg kg^{-1})**	**N_{tot} (%)**	**SSA (m^2 g^{-1})**
Soil	6.61	25.6	0.51	4.61	6.12	3.26	2.87	2.51	0.88	118
Biochar	9.42	185.2	52.4	25.9	38.5	13.5	10.1	28.7	1.51	278
Zeolite	8.11	148.1	-	17.7	12.3	45.8	1.31	2.12	0.31	78.9

Note(s): CEC: cation exchange capacity; OC: organic carbon; Ca^{2+}: exchangeable calcium; Mg^{2+}: exchangeable magnesium; Na^{+}: exchangeable sodium; P: phosphorus; K: potassium; N_{tot}: total nitrogen; SSA: specific surface area.

2.2. Soil Measurements

At the end of the experiment, soil characteristics were evaluated using the following methods: pH and electrical conductivity (EC) by 1:1 (soil: water) solution, and soil organic matter (OM) was estimated by multiplying soil OC by 1.72 (Van Bemmelen factor) [45]. Cation exchange capacity (CEC) was measured by ammonium acetate extraction [31] and the soil's specific surface area (SSA) was calculated using the ethylene glycol monoethyl ether (EGME) adsorption method [46]. The soil total porosity (TP) was determined using the following equation after the soil bulk density (BD) was measured using the clod method [47]:

$$\mathrm{TP} = 100 \times \left(1 - \frac{D_b}{D_p}\right),$$

where TP is the total porosity (%), D_b is the soil bulk density (g cm^{-3}); and D_p is the soil particle density (g cm^{-3}), which was assumed to be 2.65 g cm^{-3}.

The wet aggregate size distribution was evaluated using the wet-sieving technique. Following air drying, soils were given a 24-h tap water soak. The soil was placed on a set of sieves with sizes of 2, 1, 0.5, 0.25, and 0.053 mm, and the sieving process was carried out for 10 min at a rate of 35 vibrations per minute (along a 38.1 mm amplitude). After wet-shaking in each sieve, the residual material was carefully removed and dried at 105 °C. The weight ratio of aggregates from each filter to the total weight of aggregates was used to calculate the aggregate size distribution. Using the wet sieving data [48], the mean weight diameter (MWD) of the soil aggregates was calculated as follows:

$$MWD = \sum_{i=1}^{n} \overline{Xi}\, Wi,$$

where $\overline{Xi}$ is the average diameter of the aggregates remaining on each sieve, Wi is the weight ratio of aggregates per sieve to the total weight of the soil used, n is the number of sieves used.

Inductively coupled plasma optical emission spectrophotometry (PerkinElmer Optima 7300 V) was used to measure the quantity of soluble base cations (Ca^{2+} and Mg^{2+}), and a flame photometer was used to measure Na^{+} (M410 Sherwood). The sodium absorption ratio (SAR) was then determined using the formula:

$$\text{SAR} = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+}+Mg^{2+}}{2}}} \times 100.$$

Before removing the plant from the soil at the end of the experiment, intact soil cores (10 cm in diameter) were obtained to measure the saturated hydraulic conductivity (Ks) at 0–5 cm depth and the soil water retention curve. Pressure plate equipment and porous plate funnels were used to calculate the soil water retention curves [49]. The applied tensions were 0, −10, −33, −100, −300, −500, and −1500 kPa, respectively, which equates to 0, 2, 2.5, 3, 3.5, 3.7, and 4.2 pF (log matric potential). The field capacity (FC) and the permanent wilting point (PWP) were calculated to be −33 and −1500 kPa, respectively. There were three replications carried out. The difference between FC and PWP was used to compute the available water content (AWC). The soil water retention curve was used to determine the volume of macro-pores (>10 m), meso-pores (0.2–10 m), and micro-pores (<0.2 m), which correspond to <2.5 pF, 2.5–4.2 pF, and >4.2 pF [50]. The Ks was determined in a laboratory setting using the constant-head method at 0.1 kPa pressure by applying a steady hydraulic head to the top of water-saturated cores [51].

2.3. Plant Measurements

At the end of the growing season, the plants' height and growth were measured. After harvest, at the project's conclusion, the weight of the biomass was recorded (30 July 2020). After the project was completed, the plants were cleaned in distilled water, chopped into shoots and roots, and then placed at 70 °C until they reached a consistent weight. The root samples were first stained in methyl violet solution and then scanned by the Delta-T SCAN Image Analysis System to determine the root's length, surface area, and average diameter [52]. After the digestion and distillation processes, the total nitrogen (N) content of the shoot was determined using the titration technique with the Kjeldahl system. Flame photometry at an absorption wavelength of 766.5 nm was used to quantify potassium (K), and spectrophotometry was utilized to calculate the proportion of phosphorus (P) [53].

2.4. Data Analysis

A one-way analysis of variance (ANOVA) was carried out to determine the importance of variations in soil properties between various treatments. After the least significant difference (LSD) test at $p < 0.05$, lowercase letters in the figures denote statistically significant differences. All figures were created in Excel 2020 and all data were analyzed using SPSS 24.

3. Results

3.1. Changes in Soil Characteristics

There was a significant difference between the biochar and zeolite treatments, and adding treatments considerably altered the physio-chemical features of the soil ($p < 0.05$) (Table 2). The highest pH was associated to B10 with 1.36 units more than the control (6.53). Applying zeolite had no significant influence on the pH of the soil. All biochar and zeolite treatments considerably raised soil CEC; however, B10 induced the maximum CEC with an amount of 139 cmolc kg^{-1}. B5-related CEC came in second place with a value of 115 cmolc kg^{-1}. With concentrations of 38 and 60 cmol kg^{-1}, Z5 and Z10 revealed CEC levels that were much lower than biochar treatments. Application of biochar resulted in a considerable increase in OM, with B5 and B10 seeing increases of 50% and 93% over controls, respectively. Zeolite use did not significantly alter the OM of the soil. In comparison to the control, the soil SAR in zeolite-treated soils increased by 65% and 143%, respectively, in Z5 and Z10. The addition of biochar had no significant impact on soil SAR. In contrast, zeolite-treated soils did not substantially differ from the control in terms of soil BD; adding biochar significantly reduced the quantity of BD. B10 and Z10 significantly increased soil porosity by 33% and 22% more than the control, respectively. Additionally, B5 and B10 use resulted in considerable changes to MWD, a measure of soil aggregation, with increases of 79% and 166% in comparison to the control. Z10 application resulted in a 48% reduction in soil MWD when compared to the control. Both biochar and zeolite treatments significantly increased soil surface area and the highest surface area was achieved from soil treated with B10, which had a surface area of 315 m^2 g^{-1}.

Table 2. Soil characteristics under biochar and zeolite treatments.

	pH	**CEC (cmolc kg^{-1})**	**OM (%)**	**SAR (meq l^{-1})$^{0.5}$**	**BD (g cm^{-3})**	**TP (%)**	**MWD mm**	**SSA (m^2 g^{-1})**
C	6.53 ^{c}	24.5 ^{e}	0.87 ^{c}	3.12 ^{c}	1.42 ^{a}	41.1 ^{c}	0.68 ^{c}	116 ^{d}
B5	7.35 ^{b}	115.1 ^{b}	1.31 ^{b}	3.39 ^{c}	1.33 ^{b}	49.3 ^{b}	1.22 ^{b}	251 ^{b}
B10	7.89 ^{a}	139.2 ^{a}	1.68 ^{a}	3.88 ^{c}	1.21 ^{b}	54.8 ^{a}	1.81 ^{a}	315 ^{a}
Z5	6.68 ^{c}	38.5 ^{d}	0.91 ^{c}	5.16 ^{b}	1.41 ^{a}	47.1 ^{b}	0.61 ^{c}	170 ^{c}
Z10	6.73 ^{c}	59.7 ^{c}	0.95 ^{c}	7.59 ^{a}	1.38 ^{a}	50.2 ^{ab}	0.35 ^{d}	281 ^{b}

Note(s): CEC: cation exchange capacity; OM: organic matter; SAR: sodium adsorption ratio; BD: bulk density; TP: total porosity; MWD: mean weight diameter; SSA: specific surface area. Different lowercase letters indicate significant differences between means ($p < 0.05$).

3.2. Changes in Soil Hydrologycal Indics

The pore size distribution of the soil significantly changed after the application of zeolite and biochar ($p < 0.05$) (Figure 1). The results revealed that applying biochar at a high rate (B10) increased the proportion of soil micro-pores by 33% compared to the control. Other treatments, however, failed to significantly alter the micro-pores. When it comes to meso-pores, applying biochar at both rates resulted in a 38% and 54% increase in the proportion of pores compared to the control. Zeolite soil treatment did not significantly alter the control in this region of pores. On the other hand, a considerable increase in the zeolite rate (Z10) led to a 61% rise in the proportion of macro-pores in comparison to the control. However, applying biochar had little impact on macro-pores.

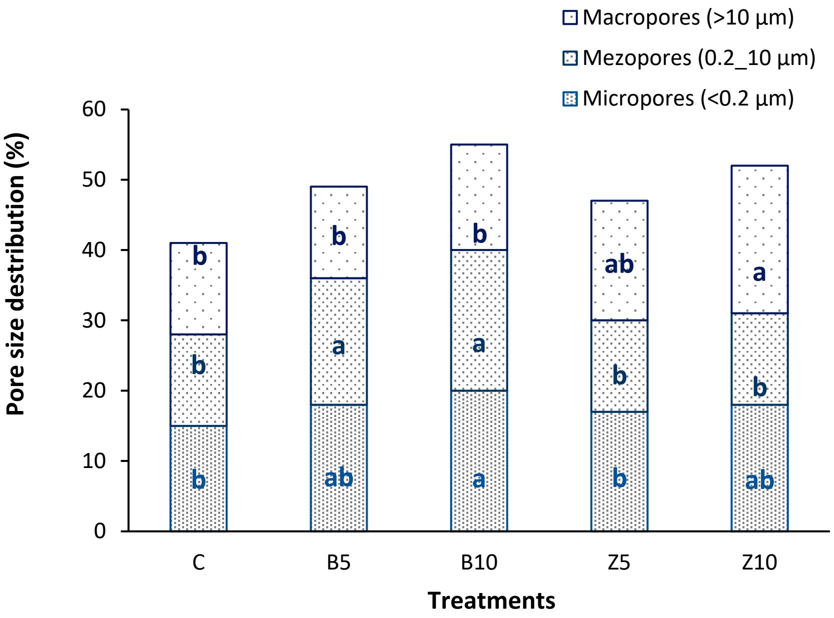

Figure 1. Effect of treatments on soil pure size distribution. Different lowercase letters with the same color indicate significant differences between means ($p < 0.05$).

Treatments and rates substantially altered the soil water retention curve ($p < 0.05$) (Figure 2). Results revealed that applying treatments had no significant impact on soil PWP; however, adding B10 caused a 47% rise in the FC point above that of the control, which was considerably significant. Furthermore, B5 significantly enhanced soil FC by 29% above the control. Although zeolite treatments increased soil FC, the effect was not significant.

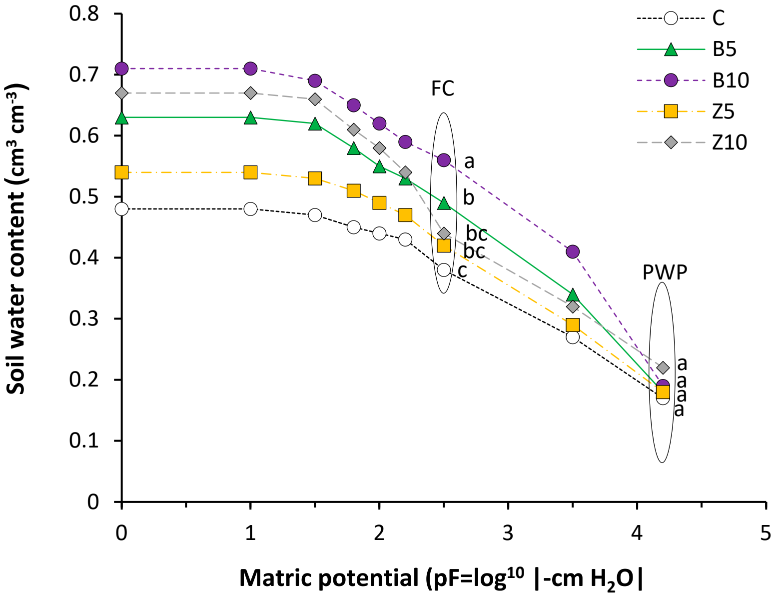

Figure 2. Effect of treatments on soil water retention curve. Different lowercase letters indicate significant differences between means ($p < 0.05$).

Treatments had a substantial impact on the soil's available water content (AWC; $p < 0.05$) (Figure 3). The B10 treatment showed the highest AWC, with a 76% increase over the control. Additionally, B5 was associated with the second-highest AWC, with a 48% increase above that of the control. There was no noticeable difference between the added zeolite at both doses and the control.

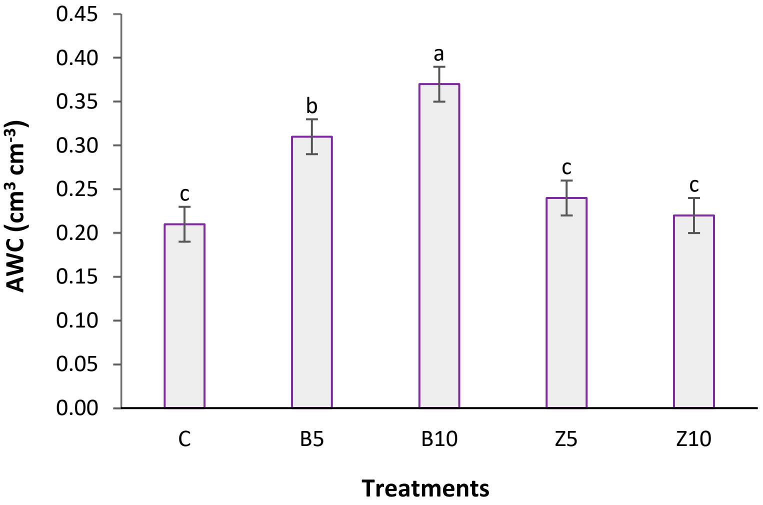

Figure 3. Effect of treatments on soil available water content (AWC). Different lowercase letters indicate significant differences between means ($p < 0.05$).

Both types of treatments had a significant impact on the soil's saturated hydraulic conductivity (Ks) ($p < 0.05$) (Figure 4). With increases of 174% and 303% over the control, respectively, the Z5 and Z10 showed the highest Ks, and there was a significant difference between them. B5 and B10, which increased Ks by 104% and 145% respectively, produced a noticeable difference from the control. Additionally, there were no significant variations across the biochar treatments.

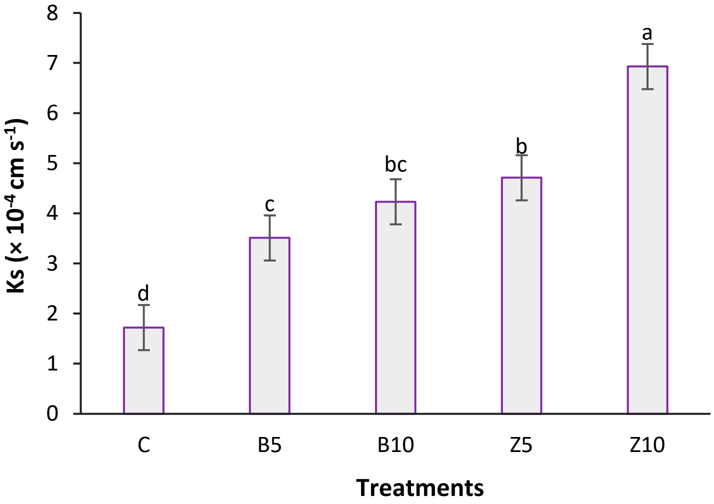

Figure 4. Effect of treatments on soil saturated hydraulic conductivity (Ks). Different lowercase letters indicate significant differences between means ($p < 0.05$).

3.3. Changes in Plant Growth

There was a substantial difference between the biochar and zeolite treatments, and adding treatments significantly altered the features of plant development ($p < 0.05$) (Table 3). Based on the findings of the root study, B10 significantly outperformed other treatments in terms of improving dry weight, total length, and root area. However, there was no discernible difference between Z5 and Z10; the application of biochar significantly increased root area and overall length. There was no discernible difference between treatments for root diameter. When biochar was added to a plant shoot analysis, the shoot dry weight rose considerably in B5 and B10, respectively, by 11% and 19% above the control. However, there was no significant variance between Z5 and Z10 and the control in terms of shoot dry weight. Similar to how zeolite treatments had little impact on shoot dry weight, they also had little impact on shoot length. On the other side, B5 and B10 significantly increased by 18% and 30% over the control, respectively. B5, B10, and Z5 significantly changed the nitrogen content of the shoots by increasing it by 113%, 179%, and 35%, respectively, in comparison to the control. Similar to nitrogen, the largest amount of shoot phosphorus was also obtained from B10 (220% more than the control). In the potassium case, B5 and B10 significantly increased the potassium levels in the shoot (55% and 90% more than the control), whereas zeolite treatments did not significantly vary from the control.

Table 3. Effect of biochar and zeolite treatments on plant growth characteristics.

	Root Analysis				Shoot Analysis				
	Root Dry Weight (g)	Root Total Length (cm)	Root Area (cm^2)	Root Diameter (mm)	Shoot Dry Weight (g)	Shoot Length (cm)	N ($mg\ g^{-1}$)	P ($mg\ g^{-1}$)	K ($mg\ g^{-1}$)
C	0.75 ^{c}	532 ^{d}	645 ^{c}	0.38 ^{a}	141 ^{c}	72 ^{c}	63.2 ^{d}	23.6 ^{d}	95.1 ^{c}
B5	0.88 ^{b}	664 ^{b}	689 ^{b}	0.39 ^{a}	156 ^{b}	85 ^{b}	134.4 ^{b}	61.8 ^{b}	147.5 ^{b}
B10	0.96 ^{a}	692 ^{a}	764 ^{a}	0.41 ^{a}	168 ^{a}	94 ^{a}	176.5 ^{a}	75.7 ^{a}	181.2 ^{a}
Z5	0.78 ^{c}	581 ^{c}	685 ^{b}	0.37 ^{a}	143 ^{c}	75 ^{bc}	85.2 ^{c}	39.2 ^{c}	101.5 ^{c}
Z10	0.85 ^{b}	605 ^{c}	694 ^{b}	0.38 ^{a}	144 ^{c}	77 ^{bc}	66.5 ^{d}	25.7 ^{d}	108 ^{c}

Note(s): N: nitrogen; P: phosphorus; K: potassium. Treatments with same letters in each column have not significant difference with each other ($p < 0.05$).

4. Discussion

Observations reveal that applying biochar as opposed to zeolite significantly changed the soil's structure, increasing the availability of nutrients, water retention, and ultimately plant growth. The improvement of soil aggregation in soils treated with biochar can be used to explain the initial cause of this modification. MWD is a crucial variable that is directly connected to the quality of the soil structure [41]. By enhancing plant rooting and ventilation, decreasing bulk density, expanding specific surface area, and increasing water availability, the MWD represents a high concentration of macroaggregates larger than 2 mm and the resistance of aggregates to degradation [14]. These factors contribute to a good soil structure for plant growth [54,55]. Additionally, the accumulation of soil organic matter is positively impacted by biochar, which can increase the quantity and availability of soil organic matter, consequently boosting the number of soil aggregates and thereafter MWD [56,57]. Soil aggregation improved as the rate of biochar increased [15]. However, the primary functional groups in biochar, including the hydroxyl, carboxyl, and benzene rings, give it a significant adsorption ability and a substantial ion exchange capacity [58]. When these unique light energy groups are combined with soil, they may absorb more organic matter from the soil solution and raise the amount of soil organic matter [59]. The biological activity in the application layer, the soil particle ratio, and the properties of soil water transport can all be improved by using some carbon-containing organic matter as a carbon source for microbial energy [60]. These are the primary causes of the boost in soil CEC and OM following the application of biochar [61]. However, the formation of bridges by cations between clay and OM particles lead to aggregation [62]. A detailed overview of the initial properties of biochar and zeolite (Table 1) reveals that the specific surface area and CEC of biochar are significantly higher than those of zeolite. These inherent qualities of biochar may emphasize the overall interaction between biochar particles and soil organic matter that led to aggregation. One of the causes of a rise in pH in soils treated with biochar may also be biochar's high CEC [63]. In fact, because there are more exchangeable sites and fewer possible acidic sites, the amount of exchangeable Al and soluble Fe in the biochar-treated soils tends to decrease [64]. In comparison to zeolite treatment, this demonstrated the ability of biochar as a soil amendment to rectify medium acidity. Numerous studies have shown that adding more biochar to the soil significantly enhances SSA [65]. This could happen as a result of the biochar's tiny pores. Fine pores in biochar with a size of 50 nm play a significant part in extending surface area [66]. This is mostly reliant on the temperature at which biochar was produced during pyrolysis. The results show that the ideal pyrolysis temperature for producing biochar with the greatest possible specific surface area is between 450 and 550 °C [58]. The temperature used in this investigation to create biochar was 500 °C. Additionally, increased sodium adsorption ratio (SAR) values in zeolite treatments indicate significant Na^+ addition to soil. It is evident from Table 1 that zeolite inherently contains far more Na^+ cation than biochar. Zeolite allows soil to provide Na^+ in exchangeable form, which then substitutes Ca^{2+} and Mg^{2+} adsorbed on the soil clays and ultimately leads to soil particle dispersion [67]. This dispersion leads to the breakdown of soil aggregation since the flocculation of clay particles is one of the fundamental prerequisites for the development of aggregates. This may possibly be the cause of the MWD decline with increasing zeolite treatment [68]. Another explanation is that when the amount of zeolite, which contains particles between 2.5 and 5 mm in size, rises, the smoothness and aggregation between the soil matrix particles declines and, as a result, the soil structure deteriorates [69]. The large amount of drainage water with rising zeolite levels during irrigation served as additional support for this hypothesis. As a result, more than 70% of the irrigation water discharged from the Z10-containing pots originated from their base. This is an obvious illustration of how the structure of the soil is destroyed when there is a high zeolite concentration.

Significant biochar addition led to the best improvement in soil overall porosity (Table 2). Additionally, certain differences emerged when the pore size distributions for zeolite and biochar were compared (Figure 1). A fundamental and important factor in soil aeration, root development, the transfer and storage of soil water and cations is pore size distribution [24]. However, zeolite enhanced the fraction of macro- and, somewhat, micro-pores; biochar treatment significantly raised the share of micro- and meso-pores. It is obvious that the smaller pores in soil structure are what keep water in the soil and prevent it from draining [70]. The presence of micro-pores helps light-textured soils hold onto water better. However, the water in the micro-pores may be kept there so firmly that it is challenging for the plants to access it. Meso-pores offer greater aeration and drainage, which makes it easier for plants to access water [71]. The application of biochar offers sufficient quantities of both types of pores to improve the soil's physical properties and boost the quantity of water that is accessible to plants [72]. The main cause of the observed increase in soil water availability (Figure 3), which is strongly affected by pore size distribution, and water content near field capacity (Figure 2), is this phenomenon [40]. On the other hand, the application of zeolite substantially enhanced the percentage of macro-pores. However, pores that do not develop capillary menisci and, as a result, do not hold water against gravity, are referred to as macro-pores [73]. Macro-pores can be found in fissures, fractures, rotted roots, earthworm channels, and interaggregate gaps [74]. In fact, a larger proportion of macro-pores in zeolite-treated soil increased hydraulic conductivity, which resulted in water loss and a reduction in the amount of water accessible to the root zone [75]. This is the primary cause of the rise in saturated hydraulic conductivity that occurred when zeolite application rates increased from Z5 to Z10 (Figure 4).

When compared to zeolite, biochar had a better effect on plant development (Table 3). This response was probably brought on by fundamental changes in soil structure, soil CEC, and nutrients contained on the biochar's surface [24]. Numerous studies have demonstrated that soil structure has an impact on plant establishment and the development of growth characteristics [76,77]. A crucial element in the stabilization of soil aggregates, the production of soil aggregates, and eventually the growth of plants, was enhanced soil structure, which also increased the OC (Table 2) [37]. In reaction to increased aggregates, plant roots can change their allocation mechanisms and they can develop in high MWD soil [78]. The key factor increasing plant root properties in biochar-treated soil is because of this. Additionally, the high surface area of biochar allows for high CEC and increases nutrient availability in soil [64]. Therefore, it is evident that plants have a greater chance of absorbing essential nutrients from biochar absorption sites in soil that has been treated with biochar. On the other hand, the amount of accessible water in the soil has a direct impact on the growth of plant weight and height [6,7]. The rate at which water percolates up larger pores increases, along with the loss of accessible water and nutrients for plant roots [9]. According to reports, adding 2 to 8 g of zeolite per kilogram of soil is enough to stop nutrient leaching in sandy loam soils caused by fast water flow [75]. As a result, Z5 has been more effective than Z10 at feeding the plant nutrients (Table 3). This is due to the water moving at the fastest rate near the center of big pores [79]. However, when positively charged surfaces are present, cation exclusion takes place [80]. Such surfaces eject cations, which then collect in the middle of pores. The average cation movement will be quicker than the average water movement because the highest water flow velocity occurs in the middle of pores [81]. While biochar treatments with micro- and meso-pores enhanced AWC and reduced the volume of irrigated water from draining, they also kept nutrients and cations close to the roots, which positively impacted plant development. Numerous studies have revealed that a greater Na^+ concentration in soils upsets the nutritional balance and interferes with the control of osmotic pressure in plant tissues [67]. Based on these findings, zeolite provided an extra Na^+ cation source to the soil–plant system in this study, increasing the Na^+/Ca^{2+} ratio [68]. The accumulation of Na^+ ions in plants would be boosted by a rise in the Na^+/Ca^{2+} ratio in the root environment, which would subsequently impact the Na+ concentration in the shoots as well as the Na^+/Ca^{2+} and Na^+/K^+ ratios of the roots and shoots [67]. The use of zeolite, however, has been shown to improve plant biomass by improving nutrient retention and preventing nutrient loss through leaching, according to certain studies [82,83]. According to earlier research, adding zeolite to heavy soils (clay loam and clay) with more tiny holes alters their size and form, improving soil structure and water transmission, which in turn promotes plant development [79]. This development will undoubtedly stop waterlogging in dense soil textures. On the other hand, adding zeolite at a high rate can significantly enhance hydraulic conductivity (Ks) in sandy loam (the type of soil utilized here) soil with bigger pores [75]. AlO_4 and SiO_4 tetrahedrals produce an open lattice structure with pores and channels as a result of the zeolite structure, which improves water mobility in the zeolite structure [83]. Therefore, by including zeolite in the soil, new water pathways may develop [80]. Thus, zeolite treatment increases hydraulic conductivity in sandy loam soils with a coarse texture [81]. Zeolite application at low rates would be acceptable in fine texture soils to reduce hydraulic conductivity and water transferability, which reduces deep percolation and soil water loss [79].

5. Conclusions

Utilizing the proper soil amendment ensures that the soil structure will improve and that the water content accessible to the plant will increase to its maximum. The findings show that, because of its unique structural characteristics, adding biochar to a sandy loam soil is obviously better than doing so with zeolite. High specific surface area, high exchange capacity, and a variety of functional groups on the surface of biochar contribute to the majority of this superiority, which in turn leads to the formation of micro and meso-pores in soil treated with biochar. Ideal circumstances for the formation and development of roots and plant growth are provided by the availability of a high percentage of water and nutrients in the fine soil pores, as well as by the enhancement of soil aggregation. The quality of soil structure, water retention, and plant development are all improved by using more biochar, although using more zeolite does have drawbacks. In fact, due to their coarseness, natural zeolite particles damage soil structure, disperse soil particles, increase water loss, and thus have a negative impact on plant development characteristics. Hence, in order to increase the effectiveness of irrigation water and agricultural fertilizers in soils with structural concerns and insufficient water supply, proper use of soil amendments at a precise application level is crucial.

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acquisition, P.K., R.D.B. and R.I.T. All authors have read and agreed to the published version of the manuscript.

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Publikace 8: Předběžná zjištění o fotosysntéze a bioakumulaci kadmia v rýži (*Oryza sativa* L.) a kukuřici (*Zea mays* L.) za použití biocharu vyrobeného ze slámy pocházející z C3 a C4 rostlin

Ghorbani, M., Konvalina, P., Neugschwandtner, R. W., Kopecký, M., Amirahmadi, E., Moudrý Jr, J., & Menšík, L. (2022). Preliminary Findings on Cadmium Bioaccumulation and Photosynthesis in Rice (*Oryza sativa* L.) and Maize (*Zea mays* L.) Using Biochar Made from C3-and C4-Originated Straw. Plants, 11(11), 1424. DOI: 10.3390/plants11111424.

Výskyt těžkých kovů v zemědělských půdách může být vážným problémem z hlediska environmentálního i z pohledu lidského zdraví. I v malém množství mohou narušovat vývoj rostlin (Amirahmadi et al., 2020). Jedním z těžkých kovů, který má negativní účinky na ekosystémy i bezpečnost potravinového řetězce je kadmium (Oni et al., 2019). Do půdy se může dostávat například prostřednictvím aplikovaných odpadních vod či minerálním hnojením. Důležitou roli při aktivitě kadmia v půdě má pH. S rostoucí hodnotou pH klesá jeho rozpustnost. Naopak při hodnotách nižších než 5 může být ve větší míře přijímáno rostlinami.

Kadmium v půdě je schopno negativně ovlivňovat délku kořenů a počet listů rostlin (Haider et al., 2021), metabolismus sacharidů (Gorovtsov et al., 2020) i fotosyntetický systém (Parmar et al., 2013). Bylo prokázáno, že biochar může imobilizovat těžké kovy v půdě a tím snižovat jejich toxicitu (Amirahmadi et al., 2020; Beesley a Marmiroli, 2011).

Rýže a kukuřice jsou považovány v lidské výživě za základní plodiny. Proto je důležité zabývat se vlivem toxicity těžkých kovů na snižování účinnosti fotosyntézy u těchto rostlin. Hlavním účelem této studie bylo zjistit, zda existuje rozdíl v účincích biocharů vyrobených z rostlin C3 a C4 (20 $t \cdot ha^{-1}$) na přenos kadmia do rostlin a na rychlost fotosyntézy rostlin rýže a kukuřice. Biochary byly vyráběny při teplotě 450 °C po dobu dvou hodin z rýžové a kukuřičné slámy. Experiment zahrnoval kromě kontrolní varianty, kterou byla neznečištěná jílovitá půda, také kadmiem kontaminovanou půdu (20 $mg \cdot kg^{-1}$).

Oba zkoumané biochary měly různé chemické a absorpční vlastnosti. Biochar vyrobený z rýžové slámy účinněji podporoval fotosyntézu rýže i kukuřice. Rovněž účinněji zabraňoval bioakumulaci kadmia do rostlin. Měl nižší poměr C/N, podstatně větší povrchovou plochu a také kationtovou výměnnou kapacitu. Použití tohoto typu biocharu se v jílovitých půdách s vyšším obsahem kadmia tedy jeví jako vhodné řešení. Závěry této práce by však měly být považovány za předběžné. Další aspekty této problematiky by bylo žádoucí ověřit dlouhodobými polními pokusy.

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Preliminary Findings on Cadmium Bioaccumulation and Photosynthesis in Rice (*Oryza sativa* L.) and Maize (*Zea mays* L.) Using Biochar Made from C3- and C4-Originated Straw

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Abstract: Understanding the structural differences between feedstocks is critical for biochar effectiveness in plant growth. To examine the efficiency of biochars with unique physiological structures in a cadmium (Cd)-polluted soil, rice and maize as C3 and C4 plants, as well as biochar generated from their residues, defined as BC3 and BC4, were utilized. The experiment involved a control and a Cd-polluted soil (20 mg kg^{-1}) without biochar application, and applications of each type of biochar (20 t ha^{-1}) on Cd-polluted or unpolluted soil. In rice and maize fields, BC3 application led to the highest value of cation exchange capacity (CEC), with increases of 162% and 115%, respectively, over the control, while CEC increased by 110% and 71% with BC4 in the rice and maize field, respectively. As compared to the control, BC3 and BC4 dramatically enhanced the photosynthetic rate (Pn) of rice by 116% and 80%, respectively, and maize by 67% and 31%. BC3 and BC4 significantly decreased the Cd transfer coefficient in rice by 54% and 30% and in maize by 45% and 21%. Overall, BC3 is preferred over BC4 for establishing rice and maize in Cd-polluted soil, as it has a lower C/N ratio, a considerably higher surface area, and more notable alkaline features such as a higher CEC and nutrient storage.

Keywords: waste management; sustainable agriculture; nutrient storage; plant growth

1. Introduction

In order to improve photosynthesis and plant growth, the application of biochar has been widely conducted in cropping systems in recent years [1,2]. Several factors increase plant photosynthesis following biochar addition, such as the higher availability of water and nutrients (especially nitrogen), the higher cation exchange capacity (CEC) and porosity of the soil, more active microorganisms, as well as the immobilization of toxic metals [3,4]. The type of feedstock and its C/N ratio is an important factor as they directly affect the forming of the porous structure and absorbent characteristics of the biochar during the pyrolysis process [4,5]. There are contemporary reports on the effects of biochar derived from different types of feedstocks on photosynthesis and plant growth [5,6]. For example, wood residues, bamboo, and plant stems are relatively hard feedstocks with a C/N ratio > 50. Consequently, their degradability in the pyrolysis process is lower than that of feedstocks such as rice hull, rice straw, or wheat straw [7]. Thereby, the potential effectiveness of biochar derived from feedstocks with a higher C/N ratio will decrease in the root zone as the number of negative charges and functional groups on the biochar surface is lower [8].

On the other hand, two main types of photosynthetic structures (C3 and C4 plants) can have different responses to biochar. C4 plants have a more advanced mechanism for photosynthesis and stabilization of atmospheric carbon dioxide than C3 plants due to their physical structure [9]. C3 plants, such as rice or wheat, fix CO_2 directly from the atmosphere and in mesophyll cells, while in C4 plants, such as maize or sugarcane, that process is conducted in specialized mesophyll and bundle sheath cells to participate in photosynthesis that is anatomically and biochemically distinct [10]. Typically, C4 plants have a 50% higher efficiency in photosynthesis rate (Pn) than C3 plants [9].

Regarding the role of soil metal toxicity in reducing plant photosynthesis efficiency, it should be noted that biochar addition to soil is also considered for preventing plants from heavy metal toxicity [11,12]. The concentration and toxicity of heavy metals have been widely considered in recent years due to the specific environmental problems they cause. The presence of heavy metals in soils, even in very low amounts, disrupts plant functions [12]. Cadmium (Cd) is one of the heavy metals that constitutes negative effects on ecosystems and food chain health [13]. Cd is entering into the soil through employing insecticides, irrigation with wastewater, and fertilization, as well as via metal retrieval industries. It has been widely shown that the presence of Cd in the soil causes reduction in plant growth, such as a reduction in root length and leaf number [14], and disturbances in the carbohydrate metabolism [11] and the photosynthetic system [3]. Prevention of chlorophyll synthesis is the main result of Cd bioaccumulation that is exhibited with biomass deficit and Pn reduction [15]. Cd stress furthermore alters stomatal movements, ion homeostasis, respiration in plants, and also prohibits the activities of enzymes [16]. Typically, the existing methods for reducing negative effects on plant growth are, however, costly and applicable to remediate small areas [12]. For example, enhanced phytoremediation of Pb-and Cd-contaminated agricultural soil with agricultural crops seemed not to be suitable in a reasonable time [17]. Furthermore, there is the risk of destruction of soil structure, disruption of soil biological activities, and environmental pollution [14]. Therefore, it is essential to provide a reliable and cheap method that minimizes contamination at low costs and is relatively fast without adverse effects on environmental health [16,18]. It has been widely shown that biochar can trap heavy metals in the soil and thus reduce their toxicity by relying on its unique characteristics such as high porosity and surface area [12,15].

It is apparent from earlier research that biochar can promote plant growth in heavy-metal-contaminated soils by immobilizing heavy metals. As a result, a main purpose of this study was to determine whether there is a difference in the effects of BC3 and BC4 on Cd mobilization, and if so, how large that difference is. Furthermore, because of their physiological variations, the response of rice and maize to Cd contamination can be interesting. However, a study comparing the responses of C3 and C4 plants to the addition of biochar has been overlooked thus far. Additionally, there has been insufficient research on the influence of homogeneous and heterogeneous biochar on the response of C3 and C4 plants. Homogeneous biochar is defined as the basic feedstock for biochar that is similar to treated plants (for example, rice straw biochar (BC3) applied to soil where rice is cultivated). Heterogeneous biochar is defined as the basic feedstock for biochar that differs from the treated plants (for example, rice straw biochar applied to soil where maize is cultivated). Therefore, we aimed to investigate the efficiency of rice and maize as C3 and C4 plants in response to the application biochars which are also produced from rice or maize straw. In this context, the hypothesis of this study was that biochars produced from C3 and C4 residues guarantee plant growth in Cd-contaminated soil. Additionally, it was expected that the application of two biochars would increase the photosynthesis rate of the plants due to its beneficial effects.

2. Results

2.1. Soil Properties

Biochar application in maize and rice fields significantly altered all soil properties ($p < 0.01$) (Table 1). The highest pH was found in BC3 + Cd-treated soil on both maize and rice fields, with a 2.51 and 3.01-unit increase in the rice field and maize field, respectively, as compared to the control. In rice fields, BC3 caused the greatest CEC value of 22.3 cmol$^{(+)}$ kg^{-1} (162% increase compared to the control). With a value of 17.9 cmol$^{(+)}$ kg^{-1}, BC4 application had the second highest CEC (110% increase compared to the control). BC3 and BC4 generated a considerable increase in CEC in the maize field by 115 and 71%, respectively, when compared to control. In the rice field, BC3 enhanced the value of exchangeable K^{+}, Ca^{2+}, and Mg^{2+} by 484, 310, and 218%, respectively, compared to the control, and in the maize field, by 196, 127, and 195%, respectively. Both BC3 and BC4 treatments significantly increased OC in the rice field, but there was no significant difference between BC3 and BC4. BC3 has the highest concentration of OC, at 2.13%. Additionally, in the maize field, the OC was highest with 2.23% after BC3 application.

Table 1. Chemical properties of soil as affected by treatments after four months (end of experiment).

Treatments	**pH**	**CEC (cmol$^{(+)}$ kg^{-1})**	**Exchangeable Cations (cmol$^{(+)}$ kg^{-1})**			**OC (%)**	**N (mg kg^{-1})**	**P (mg kg^{-1})**	**K (mg kg^{-1})**
			K	**Ca**	**Mg**				
Rice field									
Control	5.01 ^{d}	8.49 ^{c}	2.24 ^{d}	4.07 ^{d}	3.05 ^{d}	1.06 ^{b}	74 ^{c}	28.3 ^{c}	119 ^{c}
Cd-polluted	5.12 ^{d}	5.63 ^{d}	0.65 ^{e}	0.94 ^{e}	1.25 ^{e}	0.97 ^{b}	23 ^{d}	20.4 ^{d}	87 ^{d}
BC3	6.44 ^{bc}	22.3 ^{a}	13.1 ^{a}	16.7 ^{a}	9.71 ^{a}	2.13 ^{a}	168 ^{a}	68.1 ^{a}	178 ^{a}
BC3 + Cd	7.52 ^{a}	15.1 ^{b}	6.81 ^{b}	8.21 ^{b}	7.22 ^{b}	1.83 ^{a}	138 ^{ab}	54.3 ^{b}	142 ^{b}
BC4	6.09 ^{c}	17.9 ^{b}	5.32 ^{bc}	6.83 ^{bc}	8.24 ^{b}	1.94 ^{a}	136 ^{ab}	59.2 ^{a}	167 ^{a}
BC4 + Cd	6.68 ^{b}	9.21 ^{c}	4.14 ^{c}	5.49 ^{c}	5.25 ^{c}	1.71 ^{a}	103 ^{b}	47.4 ^{b}	138 ^{b}
Rice field									
Control	4.97 ^{d}	9.02 ^{c}	2.19 ^{d}	4.38 ^{d}	3.49 ^{d}	1.12 ^{c}	88 ^{c}	36.8 ^{c}	144 ^{c}
Cd-polluted	5.04 ^{d}	6.24 ^{d}	0.17 ^{e}	1.25 ^{e}	0.98 ^{e}	1.01 ^{c}	54 ^{d}	20.2 ^{d}	103 ^{d}
BC3	6.67 ^{bc}	19.4 ^{a}	6.48 ^{a}	9.94 ^{a}	10.3 ^{a}	2.23 ^{a}	169 ^{a}	67.3 ^{a}	191 ^{a}
BC3 + Cd	7.98 ^{a}	17.2 ^{b}	5.13 ^{b}	6.34 ^{b}	7.51 ^{b}	2.03 ^{a}	123 ^{b}	55.2 ^{b}	173 ^{b}
BC4	6.16 ^{c}	15.5 ^{b}	3.39 ^{c}	5.96 ^{bc}	7.04 ^{b}	1.87 ^{b}	121 ^{b}	54.9 ^{b}	179 ^{b}
BC4 + Cd	7.04 ^{b}	10.3 ^{c}	3.24 ^{c}	5.22 ^{c}	5.14 ^{c}	1.67 ^{b}	119 ^{b}	53.3 ^{b}	176 ^{b}

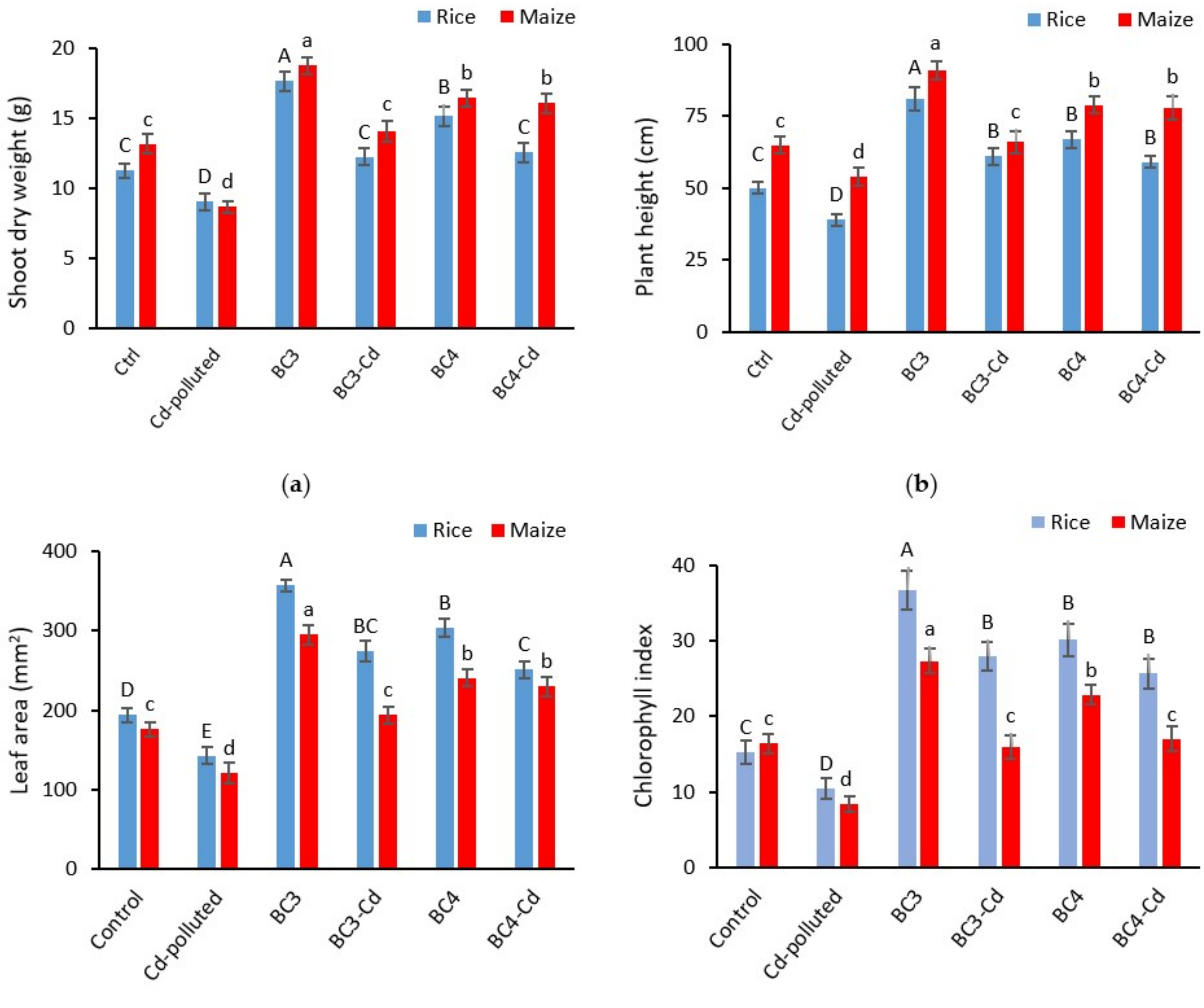
EC: electrical conductivity, CEC: cation exchange capacity, C: carbon, H: hydrogen, N: nitrogen, O: oxygen. BC3 and BC4: biochar produced from rice and maize straw, respectively. In each column different lowercase letters show significant differences of means ($p < 0.01$). The values are means from three replicates ($n = 3$). BC3: rice biochar, BC4: maize biochar, BC3 + Cd: rice biochar + cadmium, and BC4 + Cd: maize biochar + cadmium.

The highest total N levels in the rice field were associated with BC3 and BC4 application, with values of 168 and 136 mg kg^{-1}, respectively. The amount of N decreased dramatically in the Cd-polluted soil when compared to the control (69%). The concentrations of available P and K were also significantly raised when BC3 and BC4 treatments were used. The highest availability of P and K was related to BC3 with an increase of 141% and 109%, respectively, compared to the control. BC3 + Cd and BC4 + Cd showed a significant decrease in P concentration compared to their corresponding treatments (BC3 and BC4) with values of 54.3 and 47.4 mg kg^{-1}. Similar to P, values of K in BC3 + Cd and BC4 + Cd treatments were significantly lower than BC3 and BC4 with values of 142 and 138 mg kg^{-1}, respectively. In addition, the Cd-polluted treatment resulted in a substantial drop in both soil parameters (P and K) when compared to the control (with a 28% and 27% decrease for P and K, respectively).

In the maize field, the BC3 and BC4 treatments resulted in substantial differences in N, P, and K when compared to the control, as well as a significant difference between BC3 and BC4. The highest values of N, P and K were related to BC3 with a 92%, 83%, and 33% increase compared to the control, respectively. BC3 + Cd revealed a significant decrease compared to its corresponding treatment (BC3) with a reduction of 27% in N, 18% in P, and 9% in K. In addition, as compared to the control, the Cd-polluted treatment generated a significant difference in N, P, and K, with a 38%, 45%, and 28% decrease, respectively.

2.2. Plant Growth and Photosynthesis Rate

In rice and maize fields, biochar application significantly boosted plant growth metrics ($p < 0.01$) (Figure 1). In the rice field, BC3 and BC4 induced a considerable increase in shoot dry weight of 57% and 34%, respectively, and 42% and 25% in the maize field. The shoot dry weight of rice and maize was reduced by 19% and 34% in the Cd-polluted treatment, respectively, as compared to the control (Figure 1a).



(a) (b)

(c) (d)

Figure 1. Influence of biochar and Cd treatments on shoot weight (**a**), plant height (**b**), leaf area (**c**), and chlorophyll index (**d**) in rice and maize fields as representatives of C3 and C4 plants, respectively. Significant differences of means are shown by different uppercase letters for rice and lowercase letters for maize ($p < 0.01$). The values are means ± SD from three replicates ($n = 3$). BC3: rice biochar, BC4: maize biochar, BC3 + Cd: rice biochar + cadmium, and BC4 + Cd: maize biochar + cadmium.

The addition of BC3 boosted the rice height to 81 cm, resulting in a 62 percent increase above the control, while the plant height after BC4 application was 67 cm. Moreover, the maize plant height was the highest with BC3, with a value of 91 cm and a 40% increase over control. Additionally, with a value of 79 cm and a 21% increase above the control, BC4 produced the second greatest plant height. Cd-polluted treatment resulted in a significant decrease in either rice and maize plants with 22% and 17% decrease compared to the control, respectively (Figure 1b).

In the rice field, BC3 and BC4 generated a considerable increase in leaf area of 84% and 57%, respectively, and 68% and 37% in the maize field. The Cd-polluted treatment caused a significant decrease in leaf area of rice and maize by 26% and 31% compared to control (Figure 1c).

BC3 and BC4 considerably enhanced the chlorophyll content in the rice field by 140% and 97%, respectively, and the value of chlorophyll content was significantly greater with BC3 than with BC4. The chlorophyll content significantly decreased in the Cd-polluted treatment by 32% compared to the control. BC3 resulted in a considerable increase in chlorophyll content of 67% in the maize field, and BC4 came in second with a 39% gain over the control. Both BC3 + Cd and BC4 + Cd showed a significant decrease compared to their corresponding treatments (BC3 and BC4) (Figure 1d).

Rice and maize photosynthetic rates (Pn) were significantly affected by the two types of biochar ($p < 0.01$) (Figure 2). BC3 had the highest value of Pn of rice, with a 116% increase above the control. The second highest value was related to BC4 with an 80% increase compared to the control. Pn was significantly greater with BC3 (22.12 CO_2 µmol m^{-2} s^{-1}) than with BC4 (18.43 CO_2 µmol m^{-2} s^{-1}). BC3 + Cd and BC4+Cd treatments resulted in a significant decrease in Pn compared to their corresponding treatments (BC3 and BC4) with values of 17.4 and 14.5 mg kg^{-1} CO_2 µmol m^{-2} s^{-1}. Additionally, the Cd-polluted treatment showed a significant difference in Pn with a 38% decrease compared to the control. In addition, in maize, the Pn was significantly higher with BC3 than with BC4. The highest Pn value was observed with BC3 with a 67% increase compared to the control. BC4 application resulted in the second highest Pn value with a 31% increase compared to the control. The Pn in the BC3 + Cd and BC4 + Cd treatments was significantly lower compared to their corresponding treatments (BC3 and BC4). Additionally, the Pn in the Cd-polluted treatment exhibited a substantial difference, with a 61% drop compared to the control.

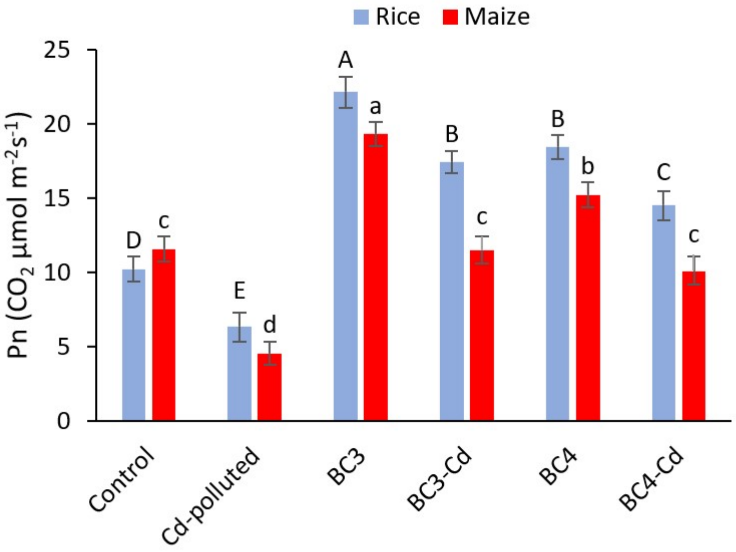


Figure 2. Effects of biochar and cadmium treatments on photosynthesis rate (Pn) in rice and maize field as representatives of C3 and C4 plants, respectively (means ± standard error). Significant differences of means are shown by different uppercase letters for rice and lowercase letters for maize ($p < 0.01$). The values are means ± SD from three replicates ($n = 3$). BC3: rice biochar, BC4: maize biochar, BC3 + Cd: rice biochar + cadmium, and BC4 + Cd: maize biochar + cadmium.

The Pn increased with the N concentration in the soil, with a stronger increase in the maize field. A positive coefficient of determination between N and Pn was obtained in the rice field ($R^2 = 0.92$) and the maize field ($R^2 = 0.43$) (Figure 3).

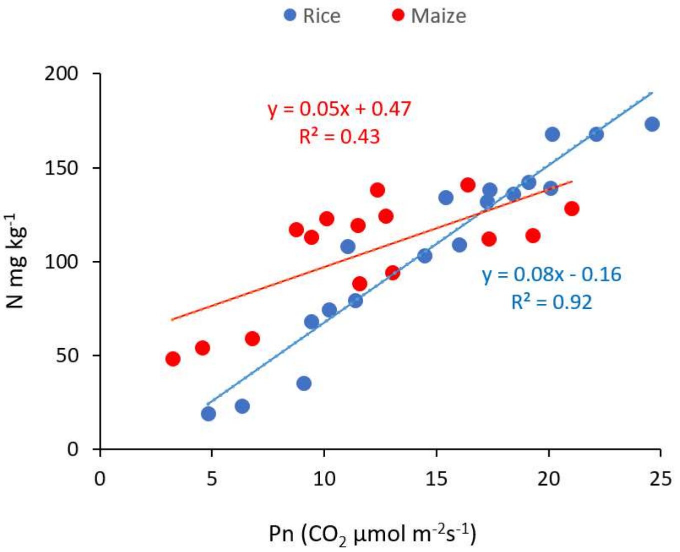
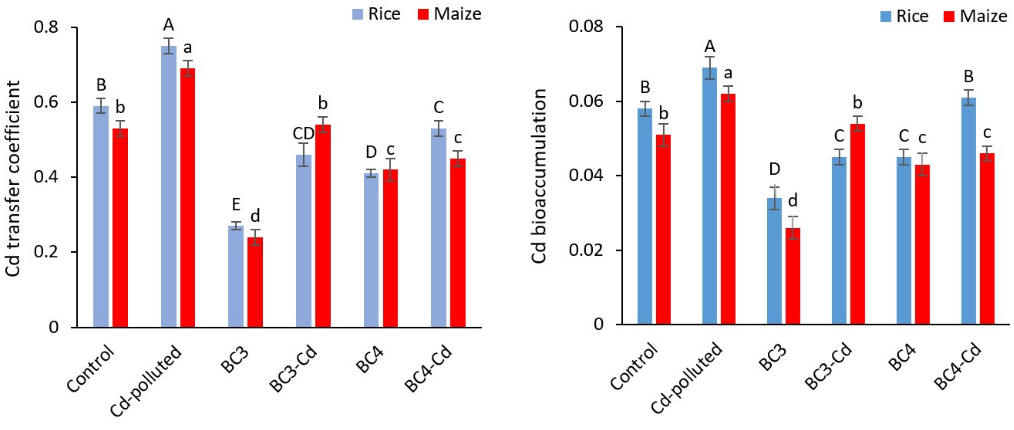


Figure 3. Effects of biochar and cadmium treatments on photosynthesis rate (Pn) in rice and maize field as representatives of C3 and C4 plants, respectively (means ± standard error). Significant differences of means are shown by different capital letters for rice and lowercase letters for maize ($p < 0.01$).

2.3. Cd Bioaccumulation Factor and Transfer Coefficient

The Cd transfer coefficient was considerably altered by biochar application ($p < 0.01$) (Figure 4a). BC3 and BC4 significantly reduced the Cd transfer coefficient in rice by 54% and 30% decrease compared to the control, respectively. With a value of 0.75, the highest Cd transfer coefficient was related to Cd-polluted treatment (27% increase compared to control). BC3 treatment resulted in the lowest Cd transfer coefficient in maize, with a 45% reduction compared to the control and BC4 had the second lowest Cd transfer coefficient, with a reduction of 21% when compared to control. Similar to rice, the maximum Cd transfer coefficient was found from Cd-polluted treatment, with a 30 percent increase above the control.



(**a**) (**b**)

Figure 4. Effects of biochar and cadmium treatments on Cd bioaccumulation (**a**) and transfer coefficient (**b**) in rice and maize fields as representatives of C3 and C4 plants, respectively (means ± standard error). Significant differences of means are shown by different uppercase letters for rice and lowercase letters for maize ($p < 0.01$). The values are means ± SD from three replicates ($n = 3$). BC3: rice biochar, BC4: maize biochar, BC3 + Cd: rice biochar + cadmium, and BC4 + Cd: maize biochar + cadmium.

Rice and maize bioaccumulation of Cd was significantly reduced after biochar treatment ($p < 0.01$) (Figure 4b). Both types of biochar reduced Cd bioaccumulation in rice, although BC3 had the lowest Cd bioaccumulation, with a 41% reduction when compared to the control. BC3, which has a lower bioaccumulation than BC4, differed significantly from BC4. In addition, BC3 had the lowest Cd bioaccumulation in maize, with a 49% reduction compared to the control. The Cd-polluted treatment resulted in the largest Cd bioaccumulation in both plants, with increases of 19 and 22%, respectively, as compared to the control.

3. Discussion

The application of biochar positively increased pH, CEC, and exchangeable cations in the experimental fields which had basically an acidic nature. As the research site is located in a tropical region and thereby generally influenced by high precipitation and temperature, it is exposed to the loss of basic cations [19]. Biochars produced from crop residues are here able to prevent re-acidification of acidic soils by boosting the soil pH-buffering capacity [20]. Large surface area of biochar with considerable functional groups (for example, carboxylic and phenolic groups) is the key factor to increasing the pH of biochar [5]. Furthermore, it contains different mineral nutrients in its ash including basic cations (K^+, Ca^{2+}, and Mg^{2+}). Therefore, biochar can potentially buffer soil pH by adding basic cations and consuming protons with negatively charged functional groups [21]. BC3 had a higher ash content compared to BC4 and consequently a higher CEC and higher values for basic cations, surface area, and pH. This is the main reason why the application of BC3 considerably better ameliorated the acidic soils than BC4 in both fields. Cd–biochar treatments significantly increased pH compared to the control. These results are in line with some previous studies which reported that using CaO-containing biochar in Cd-polluted treatment caused an increase in soil pH due to dissolving CaO and release of OH-ions into the soil solution [16,20]. In addition, the availability of N, P, and K also sharply increased in BC3 and BC4 treatments. This can be explained by the more porous structure and high surface area in BC3 than BC4. During pyrolysis, volatile compounds are released in the form of gases, which can generate a particularly porous honeycomb structure as well as increase the surface area of biochar. As a consequence, water and nutrient storage in the soil will be improved by applying biochar. In contrast, treatments that contain Cd showed negative effects on OM and N, P, and K availability. This means that Cd challenges for absorption of several mineral nutrients with the same chemical properties such as Ca^{2+} and Mg^{2+} in the root zone, thereby causing a mineral deficiency [12]. Moreover, the accessibility of nitrates, phosphate potash, and sulfates in soil, which do not have the same chemical characteristics as Cd, is prevented by the Cd bioaccumulation. A decrease in macronutrients in the tissue due to high concentrations of Cd has been reported in previous pieces of literature [16,20].

The application of BC3 to both plants significantly reduced the bioaccumulation and the transformation of Cd compared to BC4. Typically, biochar application in agricultural soil induces important surface characteristics changes due to a consequence of biochemical interplays, which are correlated with improving the adsorption behavior of cations [7]. Biochar has many functional groups such as carboxylate and hydroxyl groups [15] and has the potential for electrostatic interaction [22], ion exchange [21], and a strong surface complex with heavy metals [23]. Therefore, those intrinsic adsorbent properties in biochar play an important role in stabilizing Cd and increasing the concentration of non-absorbable Cd in the soil [21]. Thus, a decrease in Cd uptake in plants is expected [12] due to the surface characteristics of biochar [21,24]. This is the main reason why BC3 application reduced bioaccumulation of Cd in rice and maize by 41% and 49%, while the reduction with BC4 in rice and maize fields was at 22% and 16% compared to control. Next to the higher surface area and CEC, BC3 also resulted in an increase in the chlorophyll contents and photosynthesis activity compared to BC4, further supporting the higher suitability of BC3. It has been reported that biochar from rice residues caused an immobilization of Cd by 97% in the soil [15], while biochar derived from wood residues, bamboo, maize stem, and nutshells stabilized Cd less by 60% [25,26]. This can be related to the lower C/N ratio of rice husks compared to that of other feedstocks. A high C/N ratio of the feedstock causes the incomplete formation of adsorption properties at the biochar surface during the pyrolysis process and thus reduces Cd immobilization in soil [27]. The lower C/N ratio of BC3 than that of BC4 can confirm this hypothesis. BC3 also reduced the Cd transformation towards grains significantly more than BC4 which was the desired result. Moreover, it has been proven that rice husk biochar incorporation in soil provides silicon (Si) and other nutrients and improves their mobility in soils under Cd stress [15]. In fact, the addition of biochar from rice residues significantly contributes to nutrient cycling in the soil–plant system and mitigates Cd translocation and its deleterious effect on rice growth [28].

The addition of BC3 specifically increases the growth of rice and maize. The positive growth responses were attributed directly by biochar-supplied nutrients [3]. In this study, biochar BC3 provided more available nutrients (Ca, Mg, K, and N) and higher EC than BC4. The EC value represents the value of water-soluble nutrients [22]. Consequently, the improved nutrient contents in the soil such as available Ca, Mg, and K could enhance nutrient uptake and benefit plant growth [29]. Smaller shoot dry weight in Cd-contaminated treatment was probably due to the toxic Cd concentrations in plants [12], which lead to a disturbance in the metabolic processes [30]. When no Cd treatment was applied, BC3 could add sufficient nutrients into the soil. This is because of the high surface area of biochar produced from rice husk that can ameliorate Cd toxicity by stabilization of it in soil [21,24]. Increasing the plant height and leaf area resulted in an increase in the shoot dry weight due to preventing Cd uptake by plant roots. The application of biochar prevented the disruptive effect of Cd and increased the amount of chlorophyll in the leaf by decreasing the Cd bioaccumulation in the plant and the transfer coefficient.

Cd concentration in plants caused interference with the chlorophyll synthesis process, disrupting it [3]. It is also possible that biochar improves the photosynthesis of hydrocarbon materials and increases the production of biomass by increasing the amount of chlorophyll content [31].

The photosynthesis rate of both plants significantly increased with application of biochar, especially of BC3. This increase could be considered as a consequence of improving high leaf area and chlorophyll content following BC3 application. BC3 significantly increased Pn in rice and maize by 116% and 66% compared to the control, while increases in the Pn of rice and maize after the application of BC4 were at 80% and 31% compared to the control. The better performance of BC3 is related to its high surface area and nutrient storage than BC4. In biochars analyzing, the amount of N and NO_3^--N input with BC3 (218 kg N ha^{-1} and 1.96 kg NO_3^--N ha^{-1}) was consequently higher than that from BC4 (90 kg N ha^{-1} and 1.32 kg NO_3^--N more). There was a significant positive correlation between N in the soil and the Pn of rice. It has been proven that with an increase in total N in the soil and thereafter an increase in the N concentration in the plant, both a higher leaf area and chlorophyll content can be expected [3,32]. Typically, the presence of the rubisco enzyme as well as the N concentration are higher in C3 than in C4 plants [30]. It shows a larger N store in photosynthetic enzymes and a higher N demand of C3 plants than of C4 plants. Hence, the enhancement in the N uptake by the plant and the prevention of N leaching from the soil due to applying biochar [3] are helpful for boosting the photosynthesis and plant growth of C3 plants compared to C4 plants. Previous studies have shown that C4 plants tend to have lower water potential shortage and stomatal conductance than C3 plants [32]. Hence, C4 plants cannot as much use the advantages of biochar application as C3 plants, which is supported by our results of the higher biochar-induced increase in Pn for rice but lower increases in this parameter for maize.

4. Materials and Methods

4.1. Soil, Plant, and Biochar Preparation

The study was conducted in 2020 at the Agricultural Technology and Natural Resources Development Center (37°11′2.5″ N 49°39′36.6″ E) in Gilan, Iran. Some environmental parameters of study area are presented in Table 2. Rice and maize were selected as representatives of C3 and C4 plants, respectively, for the evaluation of their response to biochar application to Cd-contaminated soil. Two types of biochar were also produced from residues of the selected plants (rice or maize straw), called hereafter BC3 and BC4, by a rotary furnace. After about two hours of slow pyrolysis at 450 °C, cooking was completed by sprinkling water on the biochar (see Ghorbani et al., 2021 for details). To achieve the Cd-contaminated soil, cadmium nitrate ($Cd(NO_3)_2$) solution at 20 mg kg^{-1} soil (equal to 4.48 g per m^2 soil with a depth of 15 cm and a bulk density of 1.68 g m^{-3}) was spiked to the soil one week before planting. At the same time, biochar types were manually spread on the research field at a rate of 20 t ha^{-1} and homogeneously mixed by tractor plowing into the topsoil (25 cm). The experiment involved a control and a Cd-polluted soil without biochar application, and applications of each type of biochar on Cd-polluted or unpolluted soil. Consequently, six treatments were performed and named: control, Cd-polluted, BC3, BC3 + Cd, BC4, and BC4 + Cd.

Table 2. Environmental description of the study area.

Site Property	Description
General climate	Humid temperate continental monsoon climate
Average annual air temperature (°C)	17.2
Frost-free period (day)	250
Average annual precipitation (mm)	1359
Duration of sunshine (h $year^{-1}$)	1938.3
Parent material	Fluvial alluvium
Clay minerals	Mainly mica and montmorillonite
Soil classification (WRB)	Hydragric anthrosol
Soil tillage system	Rotation

Rice (*Oryza sativa* L.) cv. Hashemi and maize (*Zea mays* L.) cv. Single Cross 704 were grown in April 2020 in two separate fields but close to each other on the same soil with clay texture. Therefore, for each field, 18 plots including 6 treatments and 3 replications were performed (36 plots in total for both fields). Plot size was 20 m^2 (4 m × 5 m).

4.2. Soil and Biochar Analysis

According to the USDA soil taxonomy system the experimented soils were calcified in anthrosols and some soil properties were analyzed before and at the end of experiment by following methods: soil pH and electrical conductivity (EC) in a 1:1 (*w:v*) soil to water ratio; soil texture by hydrometer (Beretta et al., 2014); organic carbon (OC) by wet oxidation [33]; total nitrogen (N) by Kjeldahl [34]; and CEC by ammonium acetate extraction (Tournassat et al., 2004). Exchangeable K^+, Ca^{2+}, and Mg^{2+} were analyzed using a 5:50 ratio of soil:ammonium acetate (NH_4OA_c)-buffered solution at pH 7, in which the basic cations adsorbed in soil were replaced by $NH_4{}^+$ ions [35] and measured by spectroscope (ICP-OES, PerkinElmer). The atomic absorption method was used for Cd measuring [36] (Table 3).

Table 3. Selected properties of soil and biochar.

Property	Rice Field	Maize Field	BC3	BC4
pH	5.72	5.68	8.97	7.95
EC (dS m^{-1})	0.21	0.18	0.63	0.52
CEC (cmolc kg^{-1})	7.82	8.95	45.7	19.4
Specific surface area (m^2 g^{-1})	-	-	92.3	36.4
Organic C (%)	1.13	1.06	54.6	46.1
H (%)	-	-	2.21	3.82
O (%)	-	-	18.2	25.9
N (%)	0.67	0.56	1.09	0.64
C/N ratio	-	-	50	72

Table 3. *Cont.*

Property	Rice Field	Maize Field	BC3	BC4
NO_3^--N (g kg^{-1})	0.028	0.019	0.098	0.032
Exchangeable K ($cmol^{(+)}$ kg^{-1})	2.28	2.21	25.53	11.38
Exchangeable Ca ($cmol^{(+)}$ kg^{-1})	3.92	4.12	30.34	12.21
Exchangeable Mg ($cmol^{(+)}$ kg^{-1})	3.21	3.41	22.87	8.08
Ash content (%)	-	-	38.4	19.3
Sand (%)	8.6	9.5	-	-
Silt (%)	31.6	35.2	-	-
Clay (%)	59.8	55.3	-	-
Texture	Clay	Clay	-	-

EC: electrical conductivity, CEC: cation exchange capacity, C: carbon, H: hydrogen, N: nitrogen, O: oxygen. BC3 and BC4: biochar produced from rice and maize straw, respectively.

Biochar properties were measured as following methods: pH and EC by 1:20 (*w:v*) biochar to water ratio [37]; carbon (C), hydrogen (H), and nitrogen (N) by the elemental analyzer (Perkin Elmer 2400 II); CEC and exchangeable cations by ammonium acetate method [38]; and specific surface area by the Brunner, Emmett, and Teller (BET) procedure [39] (Table 3).

4.3. Sampling and Measurements

According to [40], the photosynthetic rate was analyzed in five selected plants per plot in week 13 after the start of the experiment using a portable photosynthesis device (Li-6400XT, NE, USA). The chlorophyll index was determined by a 508 SPAD chlorophyll meter and the leaf area was measured with the Delta-T (Divises Ltd., Hatfield, UK). After four months (at the harvest time), one square meter of plants was harvested diagonally from each plot and the height of plants was measured by a T-ruler. Harvested plants, after washing, were placed for 48 h in a 60 °C oven. Plant samples (shoots and roots) were powdered with a laboratory mill Cd analysis.

The transfer coefficient of Cd and the bioaccumulation factor of Cd were calculated by Equations (1) and (2) [36] as follows:

This is example 1 of an equation:

$$\text{Transfer coefficient} = (\text{mg of Cd in the shoot})/(\text{mg of Cd in the root}) \quad (1)$$

$$\text{Bioaccumulation factor} = (\text{mg of Cd in the soil})/(\text{mg of Cd in the plant}) \quad (2)$$

4.4. Data Analysis

The statistical analysis of the effects of two types of biochar and Cd pollution on plant growth were performed in two-factorial arrangement in a completely randomized design with three replicates. The triplicate data of selected soil properties and growth characteristics were subjected to analysis using the 2-way ANOVA test, conducted by SPSS 23.0 software. Treatment means were separated using the least significant difference test. Least-square means were used to test for significant differences among the treatments at $p < 0.01$. Linear regression analysis was performed to investigate the relationships among photosynthesis rate (Pn) and total soil nitrogen (N) using Excel 2018.

5. Conclusions

Rice and maize are considered staple crops for their uses, including food for humans and feed for animals. However, soil acidity and Cd pollution are constraints for rice and maize cultivation. In the current study, biochars derived from rice or maize residues have different chemical properties and absorbent characteristics. Biochar produced from rice straw was more efficient compared to biochar for improving photosynthesis characteristics of both rice and maize in acidic soil and for mitigating Cd bioaccumulation. In fact, it can be said that the mere use of biochar does not guarantee an improvement in plant growth characteristics under stressful conditions. In other words, differentiation of feedstocks in terms of the ratio of C/N and the degree of degradability is a determining factor in the establishment of the plant in the contaminated environment, the availability of an adequate nutritional source for the plant, and plant growth. Therefore, with regard to the wide range of agricultural products, the efficient use of rice straw biochar can be a step forward in the proper management of agricultural residues. These findings can be regarded as preliminary, and future long-term studies may shed light on additional facets of the issue.

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Publikace 9: Podpora udržitelného zemědělství a zmírnění emisí skleníkových plynů pomocí biocharu získaného z čistírenských kalů—review

Ghorbani, M., Konvalina, P., Walkiewicz, A., Neugschwandtner, R. W., Kopecký, M., Zamanian, K., ... & Bucur, D. (2023). Feasibility of Biochar Derived from Sewage Sludge to Promote Sustainable Agriculture and Mitigate GHG Emissions—A Review. International Journal of Environmental Research and Public Health, 19(19), 12983. DOI: 10.3390/ijerph191912983.

Množství odpadní vody se v celosvětovém průměru za poslední desetiletí dramaticky zvýšilo. Očekává se, že tento trend bude pokračovat a množství tekutých odpadů bude v následujících letech nadále výrazně vzrůstat (Goldan et al., 2022). V Evropské unii je trend sice opačný, ale produkce kanalizačního kalu klesá jen nepatrně. V roce 2020 bylo v EU vyprodukováno 8,7 milionů tun suchého kanalizačního kalu (Vávrová et al., 2023). Hmotnost a objem kanalizačních kalů je proto nutné redukovat.

Velmi diskutovaným tématem je likvidace kanalizačních kalů prostřednictvím pyrolýzy za současného vzniku biocharu. Kaly totiž obsahují kromě žádoucích a využitelných organických látek pestrou směs škodlivin (těžké kovy, fyziologicky účinné organické látky atd.). Technologie pyrolýzy umožňuje nejen významně minimalizovat objem čistírenských kalů, ale také likvidovat parazity a patogeny, snižovat obsah nebezpečných organických látek a také imobilizovat těžké kovy, které v čistírenských kalech mohou být přítomny (Devi a Saroha, 2014).

Biochar z tohoto materiálu se však od biocharu z lignocelulózových hmot výrazně liší. Obsah uhlíku v pevném produktu po pyrolýze kalů je značně proměnlivý, obvykle se pohybuje v rozmezí 3 až 30 % (Lu et al., 2013; Qiu et al., 2015; Waqas et al., 2014; Yuan et al., 2016; Zielińska and Oleszczuk, 2015). Biochar obsahuje živiny jako P, N, K a organické látky, které zlepšují úrodnost půdy a její mikrobiální aktivitu. Někteří autoři (např. Waqas et al., 2014) oceňují přednosti biocharu proti aplikaci surového čistírenského kalu z hlediska bioakumulace polycyklických aromatických uhlovodíků a potenciálně toxických prvků – dochází ke značné redukci těchto látek. Mnozí autoři srovnávají fyzikálně-chemické vlastnosti surových kalů a biocharu (Agrafioti et al., 2013; Liu et al., 2014). Bylo zjištěno, že těžké kovy Cr, Cu, Ni, Pb a Zn jsou fixovány, imobilizovány a zůstávají v biocharu potenciálně stabilní. I když samotná pyrolýza těžké kovy značně imobilizuje, pro kadmium to platí jen částečně.

V tomto příspěvku je formou review zkoumána příprava biocharu z čistírenských kalů a její dopady na vlastnosti půdy, zdraví rostlin, vyplavování živin a emise skleníkových plynů. K úplnému pochopení výhod a nevýhod biocharu z čistírenských kalů jako doplňku půdy jsou zapotřebí další studie a dlouhodobé praktické pokusy v terénu.

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Review

Feasibility of Biochar Derived from Sewage Sludge to Promote Sustainable Agriculture and Mitigate GHG Emissions—A Review

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Abstract: Sewage sludge (SS) has been connected to a variety of global environmental problems. Assessing the risk of various disposal techniques can be quite useful in recommending appropriate management. The preparation of sewage sludge biochar (SSB) and its impacts on soil characteristics, plant health, nutrient leaching, and greenhouse gas emissions (GHGs) are critically reviewed in this study. Comparing the features of SSB obtained at various pyrolysis temperatures revealed changes in its elemental content. Lower hydrogen/carbon ratios in SSB generated at higher pyrolysis temperatures point to the existence of more aromatic carbon molecules. Additionally, the preparation of SSB has an increased ash content, a lower yield, and a higher surface area as a result of the rise in pyrolysis temperature. The worldwide potential of SS output and CO_2-equivalent emissions in 2050 were predicted as factors of global population and common disposal management in order to create a futuristic strategy and cope with the quantity of abundant global SS. According to estimations, the worldwide SS output and associated CO_2-eq emissions were around 115 million tons dry solid (Mt DS) and 14,139 teragrams (Tg), respectively, in 2020. This quantity will rise to about 138 Mt DS sewage sludge and 16985 Tg CO_2-eq emissions in 2050, a 20% increase. In this regard, developing and populous countries may support economic growth by utilizing low-cost methods for producing biochar and employing it in local agriculture. To completely comprehend the benefits and drawbacks of SSB as a soil supplement, further study on long-term field applications of SSB is required.

Keywords: waste management; carbon cycle; GHG emissions; soil amendment; plant health

1. Introduction

Organic matter makes up about 50–70% of solid waste SS [1], which contains 33.4% protein, 6.6% lipid and 3.3% carbohydrate on an organic basis, and is highly susceptible to decomposition due to the low contents of lignin and cellulose [2]. As a result of the release of hazardous metals and organic pollutants, as well as the emission of GHGs, SS has a high potential for causing environmental deterioration [3,4]. In 2020, the volume of municipal wastewater generated annually worldwide was estimated to be 360–380 km^3 [5]. It is estimated that more than three-quarters of this amount enters surface and groundwater without treatment [6]. Drying causes the water content to decrease, leaving around 20% of the wastewater that is solid and known as sewage sludge [7]. There is not an exact amount of global SS at the moment, and all available data are presented from different countries and in different years. The estimated rate of dry solid SS on a global scale in 2018 was 45 million tons [8]. This outcome was obtained by taking into account the two billion people who were part of municipal wastewater sanitation systems with secondary treatment facilities. Therefore, managing a considerable and steadily rising amount of SS is the top priority for both developed and emerging countries. There are now many techniques to handle SS, but none of them are without drawbacks. According to their annual budgets, technological capabilities, population sizes, and rates of development, many countries often use each of these techniques. Due to a lack of legal and financial resources, SS management has received little attention throughout a considerable portion of the world (including several nations in South America and Africa). As a result, several disposal methods, including landfilling, incineration, and dumping into the sea [9,10], have been used as the easiest common practices, causing negative effects on the environment, especially through GHG emissions into the atmosphere. Strict laws in Europe have led some EU countries (such as Germany and the Netherlands) to ban the landfilling of SS [11], while 50% of SS is managed by landfilling in the United States [12]. Around 35% of SS is used as fertilizer in Europe and the United States [1,13]. In Japan, 70% of SS is managed by incineration. More than half of the SS in South Korea is dumped into the sea [14]. Additionally, the incineration of SS in Finland produced 2307 tons of CO_2-eq emissions [9]. The results of GHG emission studies in Greece showed that 2883 tons of CH_4 are released from SS landfill sites annually [10].

The Sewage Sludge Directive 86/278/EEC supports the use of SS in agriculture since it is the most promising method for utilizing this waste material due to its substantial concentrations of macronutrients and organic materials. Additionally, interest in organic farming is rising as a result of the harmful effects of conventional fertilizer on the environment [15]. Some papers show that SS has a positive effect on plant yields because of its clear macronutrient content [16]. Additionally, the majority of publications [9,17] are concentrated on the harmful impacts of SS, such as the potential transfer of viruses, pesticides, heavy metals, and other contaminants. Nitrate and other contaminants may, therefore, penetrate the soil more deeply when released without being treated [18–20].

Various feedstock are used nowadays for the production of biochar, including crop residues, woody materials, green wastes, and animal manures [21,22]. Numerous studies have been conducted on the production of biochar from SS, its characterization, and the evaluation of its impact on soil and crop qualities. Although there are reviews on the characteristics of biochar and its use in soil [23–25], a special assessment on SSB is still necessary because of its enormous potential for large-scale production and the mitigation of environmental hazards. This review combines studies on the approximate volume of the world's SS production, as well as the feasibility of using SS to support sustainable agriculture. The socioeconomic perspective of SSB production in comparison with other typical SS disposal management methods is also considered. The scope and substance of the review are summarized in Figure 1.

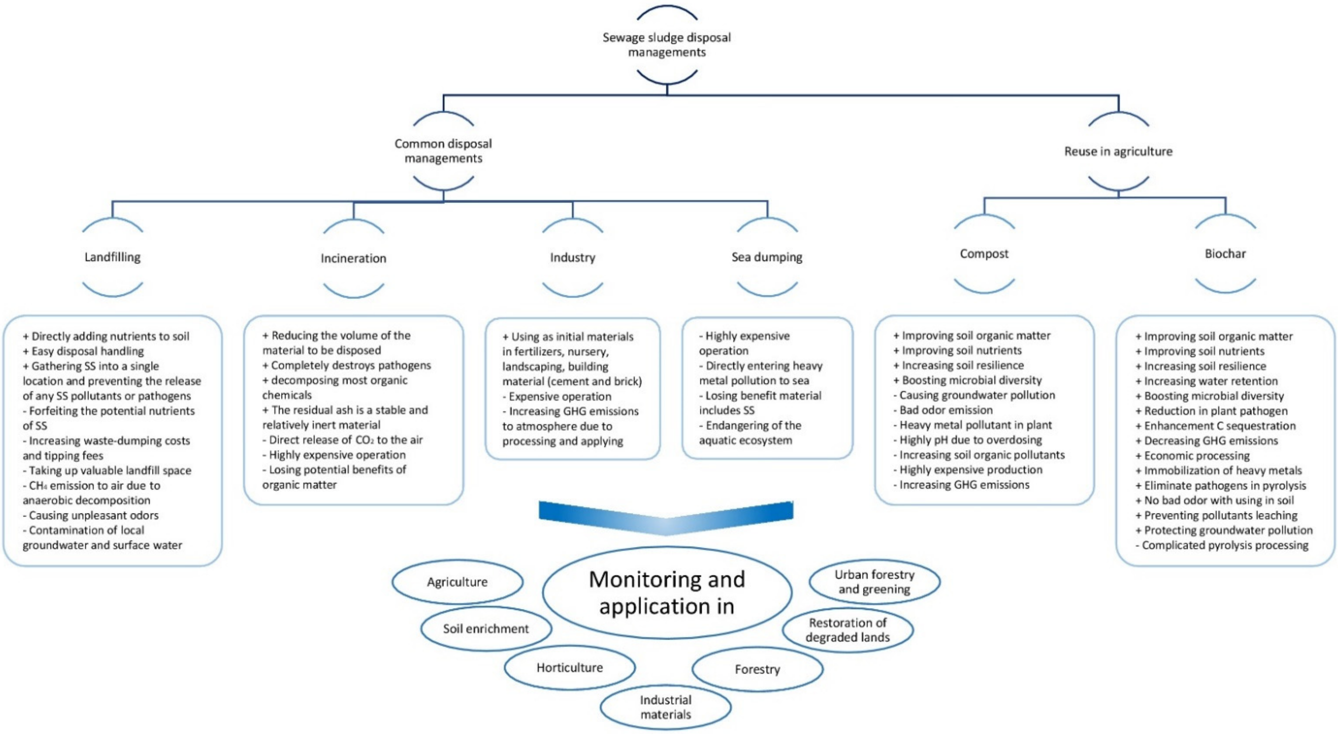

Figure 1. Summary of scope and content of the review focusing on environmental effects of common SS disposal managements compared with reuse in agriculture.

2. Importance of SS as Feedstock for Biochar Production

Sewage sludge (SS) as a huge soil C stock is a byproduct of wastewater. The presence of various pollutants, including heavy metals in SS, has irreversible destructive effects on the environment [20,26]. A significant portion of the world's SS is produced in East Asia, Europe and North America [11]. China annually produces over 13 Mt DS year^{-1} (million tons dry solid per year) of SS [27]. In the United States, annual SS production has reached almost 8 Mt DS year^{-1} [28]. Additionally, the amount of SS produced in the European Union per year was 10 Mt DS in 2006, and 11.5 Mt DS in 2015 [29,30]. Alternatively, SS could be utilized in a wide range of manners, including land reclamation, horticulture and landscaping, industrial operations, and energy recovery [31,32]. Heavy metal contamination and nutrient surpluses in SS affect organisms in more than simply agricultural soils. They also penetrate groundwater, surface waterways, and nearby ecosystems, including protected natural areas, through leaching, run-off, and volatilization [33]. Because these places are naturally uncontaminated and are typically acclimated to low nutrient supply, this can seriously damage the structure and biodiversity of organisms [34]. As a consequence, in environmental protection processes, limiting heavy metal exportation paths and preventing their development should be a top goal. The concentration of SS organic contaminants, including as heavy metals and pathogens, may have significant implications for human food safety and plant health [35]. Therefore, there is a need to improve SS treatment solutions to address the choice towards options that guarantee safety, environment protection, economic advantages, and social sustainability. The conversion of SS into biochar through the pyrolysis process can result in multiple aspects including energy production, sustainable waste recycling, the immobilization of heavy metals and organic pollutants, C sequestration, improvements in soil quality, plant development, and mitigating GHG emissions [36].

3. SSB Production and Characterization

Pyrolysis and gasification have proven to be clean and cost-efficient solutions for SS treatment [37–39]. As a result, suitable techniques of minimizing SS waste and then GHG emissions should be established. This will enhance soil functioning while also increasing carbon sequestration [40]. In many ways, converting SS to biochar can be advantageous for environment. Some of them are: reducing the volume of sludge abandoned, reducing the cost of disposal, controlling groundwater pollutants, increasing soil carbon sequestration, and reducing GHG emissions [16,41,42]. Pyrolysis and incineration, on the other hand, are two thermal processes with various extents of efficiency. Incineration is the most studied and used thermal procedures for SS treatment right now. The circulating fluidized bed is ideal for incinerating dried SS with a high heat calorific value [40]. The main advantages of this technology are high energy efficiency, and relatively low investment compared with other technologies. This technique, however, necessitates drying as a mandatory pre-treatment [43]. Furthermore, ash is created during the incineration, which can include deposited heavy metals from the SS [44]. As a consequence, it necessitates adequate treatment in order to avoid environmental damage. Pyrolysis, on the other hand, is a highly endothermic process that necessitates 100 KJel kg^{-1} DS [45,46]. This procedure also necessitates the loss of moisture. In fact, in the incineration process, SS is burned to produce energy, but in pyrolysis, energy is used to produce biochar as the final product. This could be the basic pillar for the decreased use of pyrolysis. The immediate emission of GHGs into the environment is reduced by turning the discarded SS into biochar. By applying SSB to the soil, we can expect another reduction in GHG emissions [38,42]. This mainly occurs through the increase in carbon sequestration in soil [47]. In addition, no negative effects of SSB application on the environment have been reported [48]. Table 1 summarizes the selected basic characteristics of SS and SSB produced at different pyrolysis temperatures.

Table 1. Summary of selected properties of SS and SSB.

	PT (°C)	Yield (%)	Ash (%)	P	K	Ca	Mg	C	H	N	O	O/C	H/C	C/N	pH	EC (ds cm^{-1})	SSA (m^2 g^{-1})	Ref
				(mg g^{-1})														
SS	-	-	32.8–76.14	3.4–28.4	0.54–2.05	4.04–7.4	0.57–4.1	21.6–33.2	1.24–5.2	1.32–5.74	4.4–22.5	-	-	-	5.87–7.39	2.2–4.7	1.1–7.6	[42,49,50]
SSB	300	-	-	-	-	-	-	18.6	-	3.1	-	-	-	6.00	8.65	-	-	[51]
SSB	300	-	-	-	-	-	-	22.1	-	2.9	-	-	-	7.62	7.84	-	-	[51]
SSB	500	-	-	41.1	1.61	9.71	4.32	23.4	-	3.3	-	-	-	7.09	6	-	-	[52]
SSB	300	64.3	37.4	10.4	2.25	5.33	1.35	17.1	10.3	6.2	13.4	0.78	0.60	2.76	6.2	3.3	2.88	[53]
SSB	400	56.5	49.2	11.5	2.48	5.59	1.42	15.1	9.1	4.9	7.15	0.47	0.60	3.08	7.5	0.4	7.56	[53]
SSB	500	55.3	57.4	16.6	2.75	6.01	1.68	30.1	7.7	4.3	5.91	0.20	0.26	7.00	8.1	0.5	10.8	[53]
SSB	600	53.4	63.2	18.2	2.83	6.45	2.24	26.5	7.1	3.5	5.29	0.20	0.27	7.57	10.8	0.3	12.2	[53]
SSB	700	46.6	66.6	20.1	2.91	7.8	2.56	27.2	6.9	3.1	1.63	0.06	0.25	8.77	11.9	1.3	18.3	[53]
SSB	800	42.8	68.3	19.1	3.43	8.55	2.85	26.8	6.7	2.5	1.24	0.05	0.25	10.7	11.7	0.7	19.1	[53]
SSB	900	42.2	71.2	19.5	3.35	9.14	3.19	29.2	6.6	1.2	1.16	0.04	0.23	24.3	11.4	0.4	34.2	[53]
SSB	450	-	-	-	-	-	-	-	-	1.2	-	-	-	-	8.25	1.6	-	[54]
SSB	300	-	-	42.6	2.1	8.1	8.2	21.5	9.3	5.4	-	-	0.43	3.98	-	-	4.1	[55]
SSB	400	-	-	58.8	2.4	8.4	8.4	27.5	8.1	4.4	-	-	0.29	6.25	-	-	8.7	[55]
SSB	500	-	-	59.5	2.4	8.8	8.2	26.7	7.9	3.7	-	-	0.30	7.22	-	-	10.2	[55]
SSB	600	-	-	57.6	2.8	10.4	9.3	26.1	7.3	3.4	-	-	0.28	7.68	-	-	6.3	[55]
SSB	500	-	-	-	-	-	-	-	-	1.7	-	-	-	-	8.5	5.5	-	[54]
SSB	500	-	-	-	-	-	-	26.3	-	2.6	-	-	-	10.1	7.06	0.5	-	[56]
SSB	300	-	-	-	-	-	-	22.2	8.1	3.1	-	-	0.36	7.16	8.8	-	15.6	[49]
SSB	400	-	-	-	-	-	-	24.3	7.7	3.1	-	-	0.32	7.84	8.9	-	16.3	[49]
SSB	500	-	-	-	-	-	-	20.1	7.1	2.3	-	-	0.35	8.74	9.3	-	9.43	[49]
SSB	600	-	-	-	-	-	-	22.6	6.4	1.3	-	-	0.28	17.4	10.7	-	24.7	[49]
SSB	350	-	-	-	-	-	-	-	-	-	-	-	-	-	8.72	3.04	-	[57]
SSB	300	91.1	83.2	-	-	-	-	7.53	6.78	1.3	7.13	0.95	0.90	5.79	6.43	-	5.11	[50]
SSB	500	85.7	87.9	-	-	-	-	5.63	6.48	0.7	5.21	0.93	1.15	8.04	6.96	-	15.2	[50]
SSB	700	81.2	91.9	-	-	-	-	3.96	6.29	0.4	3.36	0.85	1.59	9.90	10.5	-	13.6	[50]
SSB	450	-	-	58.2	1.78	-	-	28.1	-	3.2	-	-	-	8.78	7.22	1.73	-	[58]
SSB	450	-	-	11.1	3.01	19.9	3.59	26.2	-	1.7	-	-	-	15.4	8.54	1.1	-	[59]
SSB	500	-	-	29.2	8.01	-	-	26.1	-	2.1	-	-	-	12.4	8.06	-	-	[60]
SSB	500	54.3	73.6	54.1	9.21	8.27	0.94	18.9	6.72	2.7	4.08	0.22	0.36	7.00	7.13	-	31.8	[42]
SSB	600	51.3	77.8	59.2	10.1	9.18	1.08	18.4	6.38	2.2	1.91	0.10	0.35	8.36	11.1	-	24.1	[42]
SSB	700	48.7	79.1	63.1	10.9	9.71	1.13	18.1	6.24	1.2	0.68	0.04	0.34	15.1	12.2	-	54.1	[42]
SSB	500	50.4	68.1	58.8	14.1	6.75	1.47	23.1	6.77	3.6	4.41	0.19	0.29	6.42	7.08	-	16.3	[42]
SSB	600	46.4	70.3	64.8	15.5	6.02	1.65	23.7	6.44	3.3	2.29	0.10	0.27	7.18	11.4	-	9.01	[42]
SSB	700	43.7	74.3	68.6	16.4	7.42	1.78	22.8	6.33	2.2	0.31	0.01	0.28	10.36	12.4	-	29.9	[42]
SSB	500	54.4	69.1	54.7	12.5	1.2	1.13	22.4	6.67	3.1	4.94	0.22	0.30	7.23	7.17	-	34.2	[42]
SSB	600	51.1	70.2	53.1	13.4	1.14	1.25	22.5	6.63	2.7	4.02	0.18	0.29	8.33	11.3	-	16.2	[42]
SSB	700	49.5	72.1	56.1	13.4	1.2	1.27	21.7	6.56	2.4	3.34	0.15	0.30	9.04	12.4	-	9.21	[42]
SSB	500	45.1	64.1	96.1	1.06	1.02	3.29	26.6	7.08	3.9	4.29	0.16	0.27	6.82	7.25	-	35.7	[42]
SSB	600	43.2	63.9	92.2	1.12	1.08	2.57	27.7	6.82	3.8	3.89	0.14	0.25	7.29	8.05	-	16.2	[42]
SSB	700	40.2	68.1	95.1	1.22	1.19	2.44	27.9	6.48	2.9	0.79	0.03	0.23	9.62	13.1	-	18.1	[42]
SSB	400	-	-	-	-	-	-	25.9	-	3.6	-	-	-	7.19	7.18	0.67	-	[56]
Min	-	40.2	37.4	10.4	1.06	1.02	0.94	3.96	6.24	0.4	0.31	0.014	0.23	2.76	6	0.3	2.88	
Max	-	91.1	91.9	96.1	16.4	19.9	9.3	30.1	10.3	6.2	13.4	0.95	1.59	24.3	13.1	5.5	54.1	
Mean	-	54.4	69.4	47.8	6.0	6.7	3.1	22.4	7.2	2.9	3.9	0.3	0.41	8.7	9.1	1.5	17.6	

SS: sewage sludge; SSB: sewage sludge biochar; PT: pyrolysis temperature; C: carbon; H: hydrogen; N: nitrogen, O: oxygen, P: phosphorus, K: potassium, Ca: calcium; Mg: magnesium; EC: electrical conductivity; SSA: specific surface area.

4. Characteristics of SSB

4.1. PH

For biochars made from sewage sludge, an increase in pH is often seen as the pyrolysis temperature rises. The pH range of the biochar obtained from sewage sludge ranges from 10.0 to 13.0 at temperatures above 700 °C [42,50,53,61]. The content of inorganic components in the biochar as a result of the separation of metal salts from the organic matrix at rising temperatures, dehydration associated with a reduction in acidic surface groups during thermal treatment, and polymerization/condensation reactions of aliphatic compounds could all contribute to this increment [62]. Additionally, there is a strong positive relationship between the pH of SSB and the pyrolysis temperature (Figure 2).

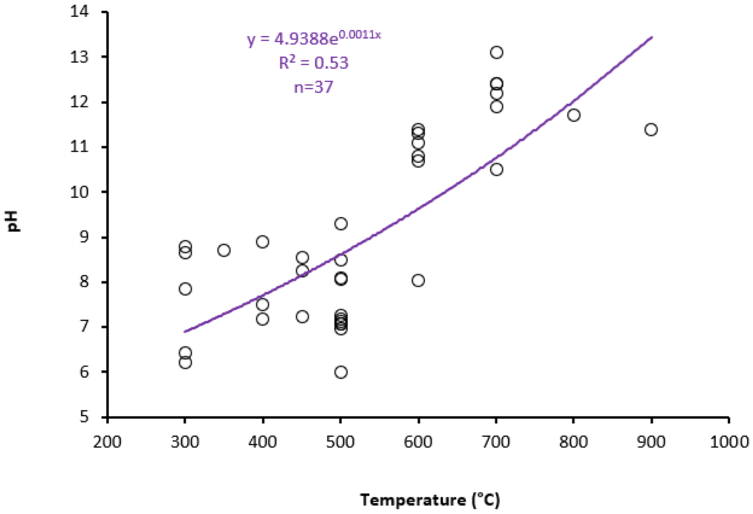

Figure 2. Regression relationships between pH and pyrolysis temperature.

4.2. Elemental Composition

C, H, O, N, P, and K are the primary components of SSB. Pyrolysis temperature and the C and H contents in SSB reveal substantial positive and negative relationships, respectively (Figure 3). Raising pyrolysis temperature often causes an increase in the C content of SSB [42]. Most noteworthy, however, is that compared with SS, C in SSB is mostly found in more stable forms. The H content of SSB reduces with rising pyrolysis temperature, in contrast to C content, and in comparison to SS (Figure 3 and Table 1). H/C and O/C ratios are useful measures for estimating the degree of carbonization and biochar production from starting materials [63]. By raising the temperature of the pyrolysis process, O and H levels fall during the moisture loss and decarboxylation processes, which lowers the H/C and O/C ratios [48]. Increased H and O loss suggests the higher carbonization of SS, higher biochar hydrophobicity, more fused aromatic ring formation, and a harder C structure [64]. The aromaticity and polarity of biochars are calculated using the molar ratios of H/C and O/C [63]. The level of aromatic C components in SSB increases when these ratios decrease. The results reveal a strong opposite relationship between pyrolysis temperature and H/C ratio (Figure 3c). The lower hydrophilicity of SSB obtained at higher pyrolysis temperatures is demonstrated by a reduction in the H/C ratio [65]. High-temperature (>500 °C), synthesized SSB is likewise highly aromatic and highly carbonized [66]. Regarding the H/C ratio, it is recommended that biochar and initial material be distinguished by a maximum value of 0.7 and that soot and biochar be distinguished by a minimum value of 0.2 [64]. The ideal H/C and O/C ratios for SSB are found at pyrolysis temperatures between 350 °C and 500 °C, according to Table 1. To put it another way, this temperature range would be appropriate for the preparation of SSB. To create a Van Krevelen diagram, molar H/C and O/C ratios of SSB obtained at various pyrolysis temperatures are utilized (Figure 3d). Biochars with O/C ratios more than 0.6 and less than 0.2 have half-lives of around 100 and more than 1000 years, respectively [64].

According to Figure 3, RHBs synthesized at various pyrolysis temperatures (most often with an O/C ratio of 0.2–0.6) have a half-life of 100–1000 years.

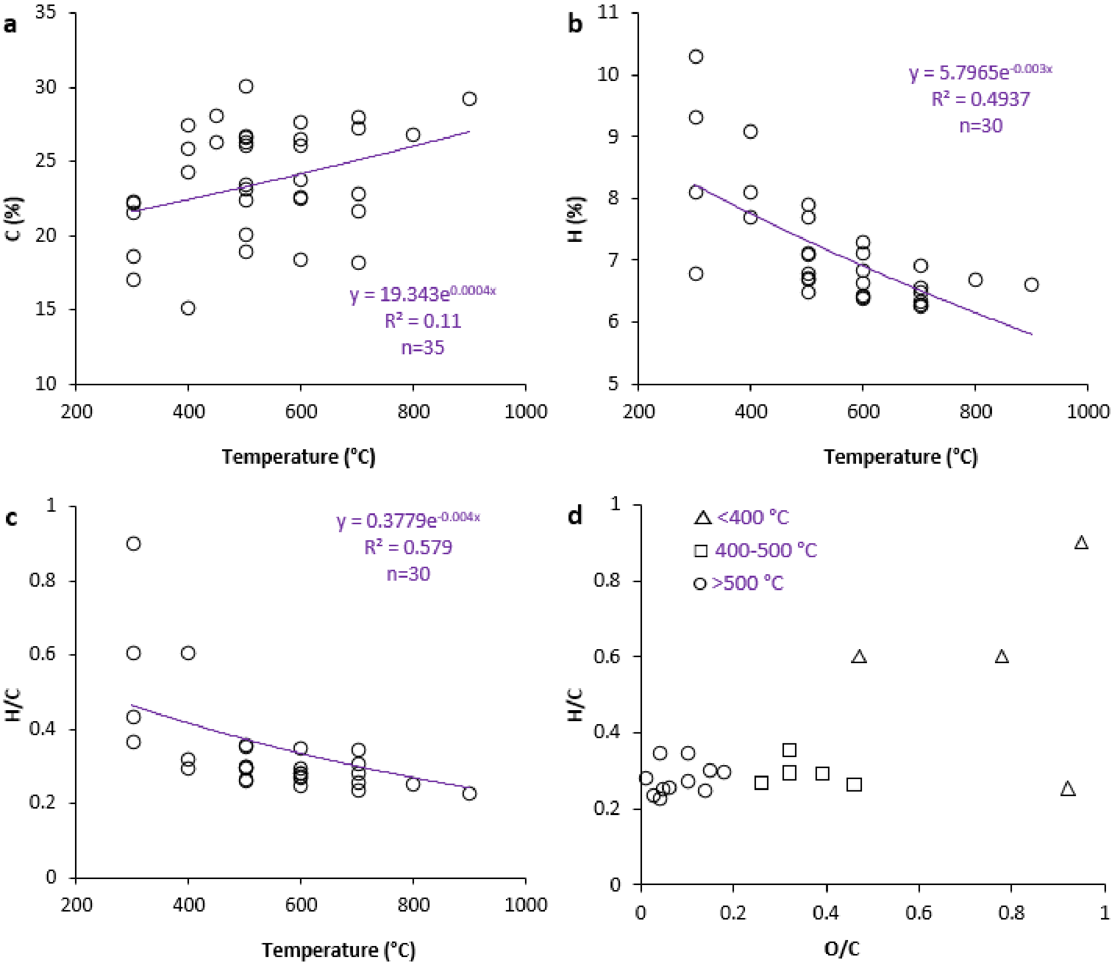

Figure 3. Relationship between traits for sewage sludge biochars and their pyrolysis temperature and Van Krevelen diagram for rice husk biochars produced at different pyrolysis temperatures. (**a**) C % vs. Temperature; (**b**) H % vs. Temperature; (**c**) H/C % vs. Temperature; (**d**) H/C % vs. O/C.

5. Sewage Sludge Biochar as Soil Amendment

Pyrolytic processes with extensive applications may be used to produce biochar for a reasonable price from a range of wastes [61]. SSB is applied as a soil additive because it has a high porosity, broad surface area, high nutritional content, and an excellent water-storage capacity [25]. A portion of the pollutants from the soil is eliminated when sewage sludge is converted into biochar, and the bioavailability and mobility of heavy metals are decreased [23]. Future developments in SSB are anticipated to concentrate on the uses for which it will be used, given that the quality and effectiveness of biochar varies greatly depending on the source material and pyrolysis circumstances [24]. A crucial factor for identifying SSB's possible application is its composition [25]. Physical and chemical characteristics of biochar can include bulk density, surface, electric conductivity, pH, cation-exchange capacity, mole ratio, concentration of different nutrients, and contaminants [37–39]. The application of SSB in the soil is a beneficial agricultural practice that enhances soil's physical and chemical properties, decreases GHG emissions, improves the efficiency of using nutrients, increases crop productivity, decreases nutrient losses through leaching, changes the content and availability of nutrients, treats contaminated soils, decreases soil erosion, and improves soil structure and fertilizer efficiency [16,41,42]. The effects of SSB application on soil and plant growth are represented in Table 2.

Table 2. Summary of selected data on SSB effects from environmental aspects.

	Effects	References
Effects on soil properties	↑ enzyme activity	[47]
	↑ pH, N, C, ↓ bioavailable As, Cr, Co, Ni, and Pb (but not Cd, Cu, and Zn)	[58]
	↑ N, P, K	[67]
	↑ pH, EC ↓ heavy metal uptake (Pb, Zn)	[59]
	↑ N, C, P, amount of heavy metals but with low availability	[68]
	↑ P, Mg, CEC, base saturation	[69]
	↑ P, EC, pH	[54]
	↑ pH, N, C, efficiency of microbial C use, ↓ content of Pb, Cd	[56]
	↑ pH, EC, enzyme activity, the concentrations of bacteria, fungi, ammonia-oxidizing archaea, and ammonia-oxidizing bacteria, immobilization of Cr, Ni, and Cd	[70]
	↑ C, soil microbial biomass, ↓ mobility of Cd,	[60]
	↑ C, N, P, K	[38]
	↑ water retention, P sorption	[71]
	↑ field capacity, wilting point, available water in coarse- and medium-textured soils ↓ bulk density	[72]
	↑ C, N, P	[73]
Effects on plant growth	↑ shoot biomass, grain yield of rice *Oryza sativa* L.	[58,74]
	↑ growth and yield of garlic *Allium sativum* L.	[66]
	↑ growth and yield of Chinese cabbage	[75]
	↑ turf grass growth	[68]
	↑ corn yield	[59,69]
	↑ biomass of *Poa pratensis* L.	[56]
	↑ biomass and yield of wheat (*Triticum aestivum*)	[54]
	↑ biomass of Chinese cabbage	[76]
	↑ grain yield of rice; no change in grain yield of wheat	[60]
	↑ dry weight of the aboveground (stems) and belowground (roots) tomato (*Solanum lycopersicum* L.); the yield was not increased significantly	[73]
Effects on GHGs emissions	↓ or ↑ CO_2 emission depending on pyrolysis temp.	[57,77]
	↓ N_2O emission and ↑ CH_4 uptake	[58]
	↓ CO_2 and N_2O emission in fertilized soils	[78]
	↓ CH_4 and N_2O emissions	[60]

↓: decrease and ↑: increase.

The functional groups of the biochar used in this study were analyzed using a Fourier transform infrared (FTIR) spectrophotometer in the mid-infrared region, from 4000 cm^{-1} to 400 cm^{-1}. The results of the FTIR spectra are shown in Figure 1.

6. Comparison between SSB and Sewage Sludge Compost (SSC) for Agricultural Purposes

Agricultural conversion attempts to advantageously utilize the organic matter and plant nutrition in biosolids, whereas landfilling and incineration constitute a one-way flow of energy and material from production to disposal [11]. Biosolids obtain the majority of their organic matter and nutrients from crops cultivated on agricultural fields [79]. Biosolids are returned to the soil by land application, where they might be used to grow new crops [80]. Composting is one of the ways of managing SS which may be widely applied in agriculture, horticulture, and forestry to restore degraded land through supplying high contents of organic matter and nutrients [1,33,79,81–83]. The process of composting is an aerobic method during which biodegradables are decayed to stable humic components with the participation of microorganisms [79,84]. The final compost product contains a high amount of decomposed organic matter with low amounts of heavy metals and pathogens compared with pure SS [79]. Sewage sludge compost (SSC) causes an improvement in soils and plants when combined with various additives (bulking agents) during the composting process, e.g., straw, bark, rice husk, sawdust, woodchips, and green and dry plant wastes [17,79,85]. SSC and SSB are rich with organic matter and nutrient storage, encouraging the growth of many beneficial microorganisms, and these organisms have a good ability to produce various organic acid compounds that help with nutrient availability or promoting plant growth [38,73,86–88]. Nevertheless, these two types of organic matter are not the same in terms of intrinsic properties and environmental impact.

6.1. Nutrient Status

SSC with rice husk resulted in substantial elevations in soil nitrogen and carbon, as well as soluble organic C [79]. Similarly, the addition of digested SS composted with sawdust and woodchips affected N content in spodosol and oxisol soils, while SSC inhibited mineral N production [85]. In contrast, SSB amendment is conductive to promoting carbon sequestration, enlarging soil carbon pools, and lessening the emission of GHGs [53]. SS contains various nutrients, especially potassium and phosphorous, which are potent fertilizer sources [89]. SSB could be a definitive source of P, and it contains a mix of inorganic polyphosphates, along with intrinsically attached P [90]. The SS becomes elevated in total P following carbonization [77]. This is due to the lower volatility of P during the carbonization process, which normally entails temperatures ranging from 300 to 900 °C in dry pyrolysis [91]. The enhancement of total P during carbonization, on the other hand, is associated with increased P fixing in ash compounds [92]. SSB contains one to two orders of magnitude more total P than SSC [93]. It has been widely shown that SSB is most effective for increasing the sorption capacity of soils, outperforming SSC [94]. Furthermore, SSC preparation takes longer and involves extra logistics compared with SSB, which is practically ready after the pyrolysis process [88]. Biochar is characterized by its higher content of stable organic carbon compounds compared with compost, and thus it slowly decomposes in the soil [68]; thus, it becomes more effective at improving the soil's physiochemical properties [25].

6.2. Plant Growth

Compost (produced from green waste and SS from municipalities) added to sandy soil in combination with biochar and plant growth-promoting rhizobacterial inoculum resulted in higher P and K availability due to greater microbial activity [95]. Soil enrichment with SSC may improve conditions for plant growth and result in slow mineralization and the slow release of micronutrients from the compost, which are taken up by plants in very small amounts, depending on the plant and soil conditions [33,34]. In addition to nutrient content, the application of SSC may also create better soil conditions through an increase in porosity and bulk density, an improvement in moisture retention and aggregation, and an increase in soil resilience due to organic matter addition [81,86]. The positive effect of a proper dose of SSC on plants has been confirmed in various species, e.g., *Mangifera persiciforma* [86], *Phaseolus vulgaris* [96], *Rhamnus* [82], and *Brassica oleracia* [97]. SSC application (once or twice per rotation cycle) considerably increased the soil content of accessible forms of copper (Cu) and zinc (Zn), which are essential for plant function, according to a study on enriched brown podzolic soil [83]. SSC increased Zn and Mn levels in grains, whilst Fe and Ni were accumulated in plant shoots [34]. It was reported that SSC addition resulted in an increase in the leaf biomass of different trees (*Quercus acutissima, Liriodendron tulipifera*, and *Betula schmidtii*) and changed the trees' physiological parameters, with the simultaneous accumulation of a safe level of heavy metals both in leaves and in soil [81]. A number of cereals, tubers, roots, and fibers show positive response to SSB addition in tropical, subtropical, and even temperate regions [73].

6.3. Heavy Metals and Pesticides

In addition to nutrients, waste may also contain harmful substances. Therefore, monitoring the quality and the dose of SSC, based on legal recommendations, is necessary prior to application thereof in the environment. Composting is a process by which environmentally harmful SS changes its properties and can be used as a soil additive, which is an important part of circularity. Composting limits the solubility and potential bioavailability of heavy metals in soils as a result of their complexation in organic matter [79,98]. However, in the context of potential contamination, e.g., by heavy metals and organic pollutants, it is important to monitor the amount and quality of SSC added to soil [99,100]. SSC and SSB, depending on their properties, may produce varying levels of bioavailable forms of potentially toxic elements (PTEs) such as Cd, Cr, and Zn when used as soil supplements [101]. With repeated applications, SS-derived PTE can contaminate the soil and accumulate in crops to levels that pose a risk to human and animal health [102,103]. In broccoli, applying SSC to the soil resulted in greater levels of Cd and Pb [104]. Swiss chard has been shown to absorb high amounts of Cu and Zn [105]. Due to its sorption mechanisms, biochar helps lower high concentrations of soluble metals such as Cd and Zn from polluted soil [25]. Heavy metals were deposited in the topsoil (0–20 cm) of barley grains following the application of SSC, according to the findings of a three-year field study on farmland soil [106]. SSC should be applied to agriculture at a low rate (150 tons per hectare), according to the authors. Likewise, it has been confirmed that fresh SSC content has an impact on the dispersion of polycyclic aromatic hydrocarbons (PAHs) in soils planted with *Festuca arundinacea*, with accumulated PAH in its tissues [99]. Although composting can effectively remove some organic contaminants from SS, the levels of some recalcitrant organic pollutants (e.g., polychorodibenzo-p-dioxins and polychorodibenzofurans (PCDD/Fs), polychlorinated biphenyl (PCBs), and perfluorinated compounds (PFCs)) sequestrated in organic fractions may even increase after organic matter decomposition [17]. In addition to the potential risk of contamination of soil and plants, SSC over-dosing can also increase pH, which may not always be suitable for all plants, as in the case of, e.g., the 45% dose of compost applied to *Rhamnus* and *Myrthus* plants [82]. From an environmental standpoint, pyrolysis is seen as a viable technology for the advantageous reuse of SS [107]. SS volume is decreased by 80% after pyrolysis, and dangerous substances such as pathogenic organisms, heavy metals, and organic and inorganic components are immobilized in biochar to prevent leaching [61]. According to reports, SSB's heavy metals are effectively immobilized at 500 °C [66]. Ass a result, the biochar produced by pyrolyzing SS does not contain harmful pathogens and is rich in nutrients and carbon [61]. SSB has drawn the attention of most researchers for minimizing heavy metal accumulate in crops [76] and its potential benefit of nourishing soil in agriculture fields [108]. The ash in SSB can have a considerable liming impact, reducing soil acidity, Mn^{2+}, Al^{3+}, and other heavy metal toxicities [91]. Various researchers have shown that biochar produced through the pyrolysis method can totally eliminate microorganisms, stabilize heavy metals in SS, and diminish mineral nutrient bioavailability [38]. In terms of pesticide filtration and carbon sequestration, biochar surpasses compost treatments [94]. SSB additions often enhance pesticide adsorption in soil, according to a wide number of studies [108]. The key parameters influencing SSB's sorption capability are its porous structure and chemical characteristics [42]. The threat of Cu, Ni, and Zn drainage from SSB-supplemented soil has been observed to be negligible [109]. Plants growing on SSC-supplemented soils acquire more PTEs [87], presumably due to compost-derived PTE's greater leaching ability [17]. As a result, it has been recommended that SSC could be used as a soil amendment in forests but not on farmland [94]. Overall, SSB as a soil amendment appears more appropriate than SSC due to its ability to immobilize and reduce PTEs.

6.4. Organic Pollutants

The use of SSC has some benefits for soils, plants, and circularity, but its introduction into the soil requires strict qualitative and quantitative control according to the limits specified in the current regulations. The microbiology of the soil could be altered by adding compost to it. SSC-treated soils had higher levels of active microbial biomass than chemical fertilizer-treated soils [87]. In a tailing environment, the enrichment of microbial community diversity and an increase in the richness of *Proteobacteria* and *Ascomycota* were found in a treatment consisting of returning alfalfa green manure and SSC [33]. SS loses pathogens that are killed in the thermophilic phase of the process by composting [79]; additionally, the use of SSC may minimize plant pathogens [110]. However, on the other hand, in addition to the many benefits of SSC, there is also an increase in chemical and microbiological risks [88]. SSC enhanced the durability of *Salmonella enterica*, which invaded some plants, demonstrating the importance of safety concerns [88]. In contrast, no negative effects on the environment have been documented in the preparation of biochar from SS. In many ways, converting SS to biochar could be helpful to the environment. Some of them are: reducing the volume of sludge abandoned, reducing the cost of disposal, controlling groundwater pollutants, increasing soil carbon sequestration, and reducing GHG emissions [111].

6.5. Processing

In addition to the economic aspects of SSC production and transport, its use in agriculture may also be limited by the risk of contamination with heavy metals, pesticides, insecticides, different organic pollutants, hormones, pharmaceuticals, and detergents, which may be included in the food chain through soil and plants [17,79,87]. On the other hand, pyrolysis is an alternative technology that is clean and cost-efficient for treating organic wastes [46]. By turning SS to biochar, the volume of SS could well be greatly decreased while also controlling environmental contaminants [112].

7. Importance of SS Conversion from the Perspective of GHG Emission Concerns

7.1. SSB Potential to Reduce GHG Emissions

There are already a number of misconceptions about how biochar affects soil nitrogen fractions [113,114]. Biochar is also being suggested as an “electron shuttle” for transferring electrons to denitrifying bacteria [115], advancing to the final phase in the denitrification. As a consequence, N_2O, as a greenhouse gas released mostly in agriculture, could be reduced. Other investigations and reviews have repeatedly verified this impact. The synthesis of bacterial N_2O reductase was boosted in a study with water-saturated soils treated with biochar, resulting in a reduction in N_2O emissions. Most of the biochar treatments, on average, decreased N_2O emissions by 13% and 38%, respectively [114]. This was observed in a variety of investigations using various feedstocks, biochar characteristics, and soil properties. Due to the application of biochar, nitrate concentrations were found to be reduced by 12% on average [116]. Similarly, a study on calcareous soil with biochar from fir sawdust revealed that emissions of soil-produced N_2O were reduced by 37–47%, implying that the breakdown of N_2O to N_2 was stimulated at the same time [117]. In fertilized soils, the reduction in N_2O emission due to SSB application even reached 87% [78].

In addition, the application of biochar to soils has mitigation potential through decreasing the emissions (or increasing the uptake) of other key GHGs. Studies of sole biochars produced from different feedstocks have shown various ability to absorb CH_4 and CO_2 emissions [118,119]. It was reported that potato stem and raspberry stem biochars were more efficient in the removal of CH_4 than wood offcut biochar and sunflower husk biochar, with lower CO_2 emissions at the same time [118]. SSB affects soil properties, e.g., increasing pH, C, N, P, K, and water retention (Table 2), thus changing the conditions for microbial activity. Improved aeration may enhance methanotroph activity through increased O_2 and CH_4 diffusion and, consequently, increase CH_4 uptake [120]. By improving CH_4 oxidation, biochar may help to offset GHGs. The impact of biochar on GHG emissions may be influenced by its properties (e.g., pyrolysis temperature, feedstock, dose), as well as the land use and soil moisture level [57,77,119–121]. Adding biochar reduced CO_2 emissions in non-saturated forest soil and improved CH_4 absorption in saturated soils [121]. Microbial tests confirmed that the stimulation of soil CH_4 uptake by biochar was correlated with methanotroph abundance in the soil [118]. This effect was dependent on how long the biochar stayed in the soil; nevertheless, it significantly increased CH_4 absorption at 60% WHC five years after the usage of the highest dose (30 Mg ha^{-1}). The presented results concern biochar produced from many feedstocks; however, the effect of SSB on soil GHG is still not fully recognized and requires further research. The mitigating effect of SSB was observed in a rice plantation, where its addition to the soil reduced both CH_4 and N_2O

emissions [58]. The effect of SSB on CO_2 emissions from oxisol was dependent on the pyrolysis temperature, and the emission rate increased after the addition of SSB produced at 300 °C and 400 °C, while it was reduced in the pyrolysis condition of 600 °C [77]. Similarly, the enrichment of luvisol with SSB resulted in increased respiration (when pyrolysis was at 400 °C), while the CO_2 emission rate was similar to the soil without the additive when added SSB was produced at 600 °C [57]. According to reports, each tonne of dry SS during dehydration and pyrolysis operation produced around 1.5 t of CO_2-eq emissions, and considering the final application approach of SSB, at least 0.3 t to 0.9 t of CO_2-eq emissions were stored as stable carbon in SSB [122–124]. In comparison, under the same scenarios, the net C outputs from conventional SS disposal managements reached at least 2.5 t of CO_2-eq emissions per t of dry SS [122]. Hence, turning SS into SSB provides many benefits for the C balance over the conventional disposal of SS. It has been reported that the main variables impacting C balance in the SSB soil system are the water and C contents of the SS and the use of dewatering agents [125]. This demonstrates pyrolysis' capacity for C sequestration and offers crucial support for the management of SS.

7.2. Comparison between SSB and Other SS Methods for Managing GHG Emissions

7.2.1. Landfilling

Landfilling is arguably the easiest approach in terms of disposal management [126]. By concentrating SS into a single site, landfilling avoids the release of any SS-borne contaminants or diseases [127,128]. During landfilling, one of the common disposal management methods, the release of GHGs is inevitable [129]. It has been proven that SS landfill is the main cause of leachate transfer to soil depth and direct CO_2 emission into the atmosphere [130]. In landfills, organic wastes decompose anaerobically, releasing methane (CH_4) gas, which could be discharged into the atmosphere [131]. Other gases emitted by landfills can emit offensive scents. It has been reported that landfilled SS may also cause emissions of 60.6 kg CH_4 t^{-1} [131]. Low access to oxygen and low initial humidity play an important role in intensifying GHG emissions [67,132]. In an anaerobic environment, methanogens are a main determinant of CH_4 synthesis. A shortage of oxygen characterized by the rapid decomposition of organic matter during the thermophilic phase (20–50 °C) near the deposited SS results in anaerobic areas [133]. However, N_2O is the culmination of a number of reactions that include denitrification and partial nitrification during the conversion of NH_3 to NO_2^- [134]. The results of GHG emission studies in Greece showed that 2883 tons of CH_4 are released from SS landfill sites annually [10].

7.2.2. Incineration

Incineration, as a common disposal management method, plays a major role in the direct release of CO_2 into the atmosphere [1,9,10,18]. Incineration produces CO_2 and also other volatile contaminants into the atmosphere [135,136]. To remove fine particle matter (fly ash) and volatile impurities from flue gasses, incinerators require complex systems [137]. SS incineration, which requires an oxygen-rich condition for the combustion of organic matter, results in CO_2 emission [129]. As a consequence, incineration is one of the costly SS removal alternatives. In Japan, 70% of SS is managed by incineration [138]. For example, the incineration of SS in Finland produced 2307 tons of CO_2-eq emissions [9].

7.2.3. Composting

In addition to the risks of SSC application to soil, an environmental problem is posed by the emission of GHGs during the composting process. The addition of magnesium chloride is recommended for reducing GHG emissions and conserving N during SS composting [139]. Composting may result in the release of about 10–15% of GHGs [140]. For example, about 26,326 kg CO_2, 54 kg CH_4, and 0.37 kg N_2O t^{-1} SS can be emitted via composting [141]. CO_2 emissions are unavoidable during composting when organic matter mineralization, temperature, and pH are considerable [142], while CH_4 and N_2O emissions are major GHGs. However, earlier research has shown that through organic waste composting, more than 30–40% of total organic carbon and 70–74% of initial total nitrogen are dissipated [143]. The majority of total organic carbon is dissipated in the form of CO_2 emissions [144], whereas 10–46% of total nitrogen is released in the form of NH_3 [145], and 0.1–10% in the form of N_2O [146]. In addition, CH_4 emissions are a consequence of anaerobic decomposition during composting [147]. Furthermore, it has been noted that when composting material settles and some anaerobic pockets form inside the material, between 0.01 and 0.03 percent of the initial total organic carbon is released in the form of CH_4 [148].

7.2.4. Industrial Recovery

The reuse of SS as building materials (such as bricks and cement) is a method for the industrial recovery of SS and disposal management [149]. GHG emissions from the production of bricks and cement are 36.5 and 89,015 kg CO_2-eq t^{-1} SS, respectively [141]. Around 35% of SS is used as fertilizer in Europe and the United States [1,13]. Approximately 3269 kg CO_2-eq t^{-1} is produced in the process of converting SS into fertilizer and using chemical raw materials such as H_2SO_4, NaOH, and NaClO. The application of the produced fertilizer also has the potential for CO_2-eq emissions of as much as 31,125 kg t^{-1} of SS.

8. Socio-Economic Potential of SSB

Because of the advantages of using biochar, it is vital to think about the financial elements of its production and use. In practice, biochar is thought to be less expensive than other waste disposal methods [150]. It has been reported that the price of feedstock (USD 6.71–110/ton) for the production of biochar from a variety of sources, such as agricultural waste, wood residues, SS, and others, is significantly less than the cost of its production (USD 51–5668/ton), which includes labor, storage, and other costs [151]. While the expense of disposing of SS in landfills is assessed to be USD 195,000 per t per year [152]. The expected market price for produced SSB is roughly USD 246/ton, which is considerably cheaper than the cost of manufactured activated carbon (USD 1500/ton) [153]. At this cost, annual expenses are covered by the proceeds from the sale of biochar. Additionally, a significant and long-lasting invisible advantage of SSB is the avoidance of the costs associated with treating, transporting, and disposing of bio-waste, as well as any potential environmental risks [154]. On the other hand, its manufacture allows for the use of a variety of feedstocks, including SS, biowastes such as food waste [65], and fermentation residues from a farm's biogas station [155], all of which contribute to the implementation of a circular economy. According to reports, landfilling does not require a significant financial investment, but it does produce gas emissions, odors, and the pollution of subsurface water [156]. Pyrolysis and incineration are both energy-intensive, reduce SS volume, and destroy pathogens and odors; however, pyrolysis is less polluting and results in nutrient buildup in biochar. Given the advantages of applying SSB to soil, which include increased yields and lower GHG emissions, this is an essential choice from both an environmental and agricultural standpoint. It is also worth mentioning that the environmental impact of SSB applications is influenced by the scope of study, as long-term field tests may yield better results than more frequent short-term laboratory studies, which come with their own set of expenses [150]. Drying, storage tanks, pyrolysis reactors, cyclones, condensers, and transport are all included in the expenses of SSB production phases [157]. Biochar production involves similar phases regardless of the feedstock utilized, which define stage-specific prices. Storage, drying, post-processing, and storage are usually the next steps after the substrate is delivered to the production site and before biochar is applied [158]. Because substrate availability and local variables have such a big impact on production costs, their contribution to the overall budget varies depending on the biomass and process circumstances. Overall, the current challenge is to find ways to reduce the cost of producing biochar and improve its economy at various stages, such as using arboricultural arising, reducing transportation costs by producing biochar on a smaller scale near feedstock sources and application sites, or using closed circuits, such as using the heat from a biogas combustion engine for pyrolysis [155,159,160]. Because the cost of the feedstock is such a large part of the overall cost of producing biochar, it is economically reasonable to use waste such as SS. Synthesis gas and bio-oils are among the bioenergy products of the pyrolysis process. Breaking the bonds that bind the molecules of biomass together is necessary to extract the chemical energy that is present in the biomass [161]. Synthesis gas is primarily made up of CO and H_2, with a little amount of CO_2 and other molecules. It burns readily and has a lower energy density than natural gas [162]. Synthesis gas can be utilized as a standalone energy source (for example, in gas turbines) or as an ingredient for synthetic natural gas, petroleum, or liquid fuel. The other bioenergy product is bio-oil, which can be used as a substitute for fuel oil or heating oil [163]. According to reports, the yields of SSB, tar, and syngas during pyrolysis conditions are roughly 56%, 26%, and 18%, respectively [164]. Fast pyrolysis, which occurs at high temperatures (500–1000 °C) and rapid heating rates (>2 C s^{-1}), releases a significant amount of bio-oil (75%), biogas (13%), and biochar (12%) [165,166]. The resulting co-pyrolysis gas' heating value was observed to be significantly higher than that of natural gas, and it also contained no measurable hazardous fumigants. To save energy and reduce potential tar and tail gas pollution, the produced tar and syngas, with heat values of approximately 17–36 MJ kg^{-1} [164] and 11–22 MJ kg^{-1} [167], respectively, were recycled as fuel alternatives for the pyrolysis process [168]. However, due to SS's high humidity, pyrolyzing it by itself is not an energy-efficient process. Dewatering before pyrolysis could significantly lower the energy required. Due to their abundant energy supply, waste agricultural plastic films can be utilized to complement this approach. Plastic films are usually applied in soil fumigation [169]. They are mostly buried in landfills, which is costly, inefficient, and destructive for the ecosystem. If SS is co-pyrolyzed with high-energy-density substances, such as plastics with energy densities ranging from 33 to 46 MJ kg^{-1}, it is predicted that the pyrolysis will become actively sustainable without the need for external energy. Co-pyrolyzation could also create extra electricity to achieve farm operations' energy needs [167].

9. Approximate Prediction of Global SS and CO2-eq Emissions from it in 2050

In recent decades, population growth has played an effective role in the production of SS [18]. Annual SS productivity and population increase were shown to have a Pearson correlation coefficient of more than 0.75 ($p < 0.01$), which indicates the inevitable effect of population growth on SS production [14]. Additionally, a correlation higher than 0.8 ($p < 0.01$) between population density and total GHG emissions was reported in [18]. To calculate the worldwide CO_2-eq emissions emitted from SS, we used the world population as a basis. There are two reasons for this: (1) Despite a limited number of case studies, data on SS production capacity and disposal management from many developing and undeveloped countries have not been reported due to a lack of thorough studies. For example, a clear capacity of annual SS production is not available in populous countries such as Nigeria, Ethiopia, and Egypt in Africa, and Indonesia, Pakistan, and Bangladesh. (2) Some developed countries have not provided a new assessment of annual SS production in the last seven years [30]. CO_2-equivalent calculations could be used to calculate the global warming potential (GWP) of three greenhouse gases (CO_2, CH_4, and N_2O). It is simple to compute the total quantity of CO_2-eq emissions produced by using the coefficients of 1, 25 and 298 CO_2-eq emissions for CO_2, CH_4, and N_2O, respectively [29]. To evaluate the current global capacity of SS in CO_2-eq emissions and to estimate the capacity for 2050, we must first determine the total volume of SS produced globally. Then, by considering different management methods and the amount of CO_2-eq emission in each approach, the total CO_2-eq emissions emitted worldwide from SS can be calculated.

According to statistics, the world's population at the end of 2020 was 7.8 billion, and this figure is predicted to rise by roughly 20% by 2050 [170,171]. Average wastewater and SS production per capita and day are predicted to be 246 L and 0.04 kg (dry solid), respectively [172,173]. Based on hsistorical data from different countries and previous studies, the contributions of disposal methods to annual SS production were assumed as follows: 26 to 70% by incineration (average 48%); 20 to 28% by landfill (average 24%); 14 to 20% by land application in agriculture, horticulture and forestry (average 17%); and 7 to 15% by other methods such as sea dumping, producing building material, and so on (average 11%) [1,16,38,45,69,174–176]. The potential of four routes of SS management for CO_2-eq emission by tons CO_2-eq t^{-1} DS (t CO_2-eq t^{-1}) were considered as follows: 223.02 t CO_2-eq t^{-1} by incineration, 1.564 t CO_2-eq t^{-1} by landfill, 31.125 t CO_2-eq t^{-1} by land application, and 93.731 t CO_2-eq t^{-1} by other management methods [142]. Then, for each continent, the proportion of the four SS management methods to CO_2-eq emissions was computed as follows:

$$\mathrm{CO_2\ t^{-1}DS} = \mathrm{M_1}(223.02) + \mathrm{M_2}(1.564) + \mathrm{M_3}(31.125) + \mathrm{M_4}(93.731) \tag{1}$$

where M_1, M_2, M_3, and M_4 represent the contribution percentages of incineration (48%), landfill (24%), land application (17%), and other management methods (11%), respectively.

Figure 4 is a schematic prediction of SS production in million tons of dry solid per year (Mt DS $year^{-1}$) of CO_2-eq emissions in teragrams (Tg) in 2020 and 2050, according to the latest statistics of continental population distribution.

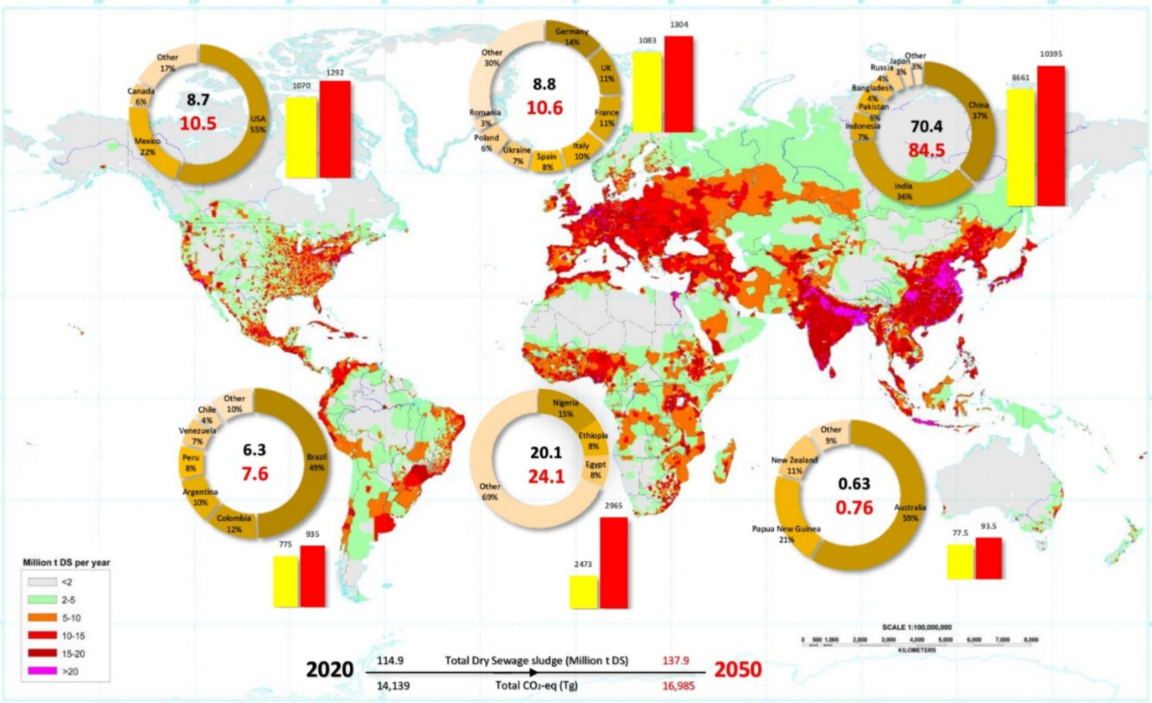

Figure 4. Global map of SS production and CO_2-eq emissions from it. The inset doughnut graphs show the share of SS-producing countries by percentage from 6 continents (North and South America, Europe, Asia, Africa, and Oceania) in 2020. The inner bold numbers of the doughnut graphs indicate the total SS produced in 2020 (black), and the predicted values for 2050 (red) in million t DS. The bar graphs show CO_2-eq emissions from different SS managements in 2020 (yellow) and the predicted values for 2050 (red) in Tg CO_2-eq t^{-1} DS.

Based on population statistics [170] and the mean capacity of SS produced per capita [171], the estimation has been made that about 115 Mt DS was produced worldwide in 2020 (Figure 2). Hence, in 2050, this figure will reach 138 Mt DS, due to a 20% increase in world population [170]. Predictably, an increase in CO_2-eq emissions is inevitable, so that the CO_2-eq emission of 14,139 Tg in 2020 will reach 16,985 Tg (20% increase) in 2050. With 70.4 Mt DS, Asia was the world's greatest producer of SS in 2020. This figure will increase to 84.5 Mt DS by 2050. Moreover, 73% of all Asian SS is produced by China and India, with one-third of the global population [170]. According to calculations, the total CO_2-eq emission value in Asia was 8661 Tg in 2020, which will increase to at least 10,395 Tg in 2050.

Following Asia, Africa was the second-largest producer of SS in the world with 20.1 Mt DS and 2473 Tg CO_2-eq emissions from it in 2020. These amounts could reach 24.1 Mt DS of SS and 1235 Tg CO_2-eq emissions by 2050. Nigeria, Ethiopia and Egypt, the three most populous countries in Africa, produce 31% of the continent's SS. The other African countries have an almost equal share of SS production. Europe and North America have an almost equal share in the production of SS and, consequently, CO_2-eq emissions in 2020 and 2050. The calculated SS production and CO_2-eq emissions for these continents in 2020 are about 8.8 Mt DS and about 1070 Tg CO_2-eq, respectively. These numbers will increase to 10.5 Mt DS and 1300 Tg CO_2-eq emissions in 2050. More than 50% of North American SS and CO_2-eq emissions are produced by the USA. Based on estimates, in 2020, South America generated 6.3 Mt DS of SS and 775 Tg CO_2-eq emissions, with 7.6 Mt DS and 935 Tg CO_2-eq emissions forecasted for 2050. In South America, Brazil is responsible for half of this quantity. Finally, Oceania can be recognized as the producer of the lowest SS and the corresponding emissions in the world with 0.63 and 0.76 Mt DS of SS in 2020 and 2050, respectively, and about 78 and 94 Tg CO_2-eq emissions for the same years.

Based on population calculations, the seven major populated countries of the world, i.e., China, India, the United States, Indonesia, Brazil, Japan, and Russia, have potential to produce half of the world's SS and are responsible for CO_2-eq emissions from it [7]. This illustrates how crucial it is to take sewage sludge management seriously in risky countries, and by adopting ecologically friendly techniques such as biochar production in densely populated regions, the amount of GHG emissions will be greatly decreased.

10. Conclusions

Sewage sludge management strategies should be adopted based on correct facts, such as population, local economy, and global view. Countries' economic conditions, population growth rates, and adherence to international regulations all have a part in determining which technical approaches should be used for sewage sludge management. This review estimated that, based on current disposal managements, CO_2-eq emissions derived from sewage sludge will rise to 24% in 2050. However, 50% of sewage sludge and related CO_2-eq emissions are produced by the seven most populous countries in the world, and there is no doubt that governments, particularly in high-risk countries, should implement mandatory sludge-management enforcement standards. Developing countries can also contribute to economic growth by using low-cost technologies such as biochar production for agriculture in the region, as well as appropriately managing sewage sludge and minimizing GHG emissions. To achieve this purpose, environmental monitoring institutions must be mobilized, public awareness must be raised, particularly among farmers, and stringent global regulations must be enacted. Comparing this waste management method to other options already in use, such as incineration, or direct use in agriculture, the conversion of sewage sludge into biochar can be more effective. Sewage sludge biochar is of importance because it provides a variety of purposes, including isolating (sequestering) carbon in the soil, lowering GHG emissions, enhancing soil quality, and acting as a preventative measure for environment degradation. Sewage sludge biochar appears to have better soil amendment potential than sewage sludge compost because of its capacity to immobilize pathogens and heavy metals and inhibit plant uptake. Despite these findings, a careful approach necessitates long-term research into crop responsiveness, soil types, and varied environmental variables. Such research will aid a better understanding of the risks associated with employing SS-derived biochar as a soil conditioner.

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Abbreviations

SS: sewage sludge; SSB: sewage sludge biochar; SSC: sewage sludge compost; GHGs: greenhouse gas emissions; CO_2-eq: CO_2-equivalent; Mt DS: million tons dry solid; Tg: Teragram.

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Publikace 10: Modifikovaný biochar—nástroj pro čištění odpadních vod

Kopecký, M., Kolář, L., Konvalina, P., Strunecký, O., Teodorescu, F., Mráz, P., ... & Bucur, D. (2020). Modified Biochar—A Tool for Wastewater Treatment. *Energies*, *13*(20), 5270. DOI: 10.3390/en13205270.

Protože se fosfor v půdách vyskytuje v malém množství, anebo v rostlinám nepřístupných formách, může být limitujícím prvkem rostlinné produkce (Cleveland et al., 2013). V rozvinutých zemích je proto samozřejmostí využívání minerálních hnojiv. Ložiska koncentrovaných fosfátů jsou však omezena. Je tedy třeba nakládat s fosforečnými zdroji racionálně (Cordell et al., 2009).

Na druhé straně je globálním problémem eutrofizace životního prostředí, zejména povrchových vod (Le Moal et al., 2019). Z velké části je za ni zodpovědné právě nesprávné používání zemědělských hnojiv, obzvláště fosforečných. Ačkoli se v zemědělství používá obrovské množství těchto hnojiv, rozhodně není zemědělská produkce jedinou cestou, kterou se fosfor do životního prostředí dostává. Člověk denně prostřednictvím moči vyprodukuje průměrně 1 g čistého fosforu (Vinnerås et al., 2006). V domácnostech je používána řada produktů (zubní pasty, prací prášky) obsahujících fosfor, který končí v odpadních vodách. V průměru tedy na jednoho člověka připadá zhruba 2,3 g fosforu za den (Comber et al., 2013).

V kalových hospodářstvích čistíren městských odpadních vod vzniká po anaerobní stabilizaci kalu voda kalová obsahující až stovky miligramů fosforu v jednom litru. Běžné jsou koncentrace nižší, obvykle v rozmezí 2,5–27 mg fosforu$\cdot l^{-1}$ (Sýkorová et al., 2014). Je tedy zřejmé, že městské odpadní vody představují zdroj P, jemuž je třeba věnovat pozornost a je nezbytné fosfor v maximální možné míře recyklovat.

Technologií k odstranění či recyklaci fosforu z odpadních vod je vyvinuto mnoho. V této studii byla testována metoda, při které byl pro recyklaci fosforu z kalové vody využit modifikovaný biochar (nasycený roztokem $FeCl_3$ a poté neutralizovaný roztokem NaOH). Kromě toho byly testovány agrochemické vlastnosti kalové vody z komunální čistírny odpadních vod a struvitu.

Potvrdil se předpoklad, že z agrochemického hlediska je kalová voda nejlepším zdrojem fosforu pro zemědělské plodiny. Přesto její použití v mnoha zemích komplikují právní předpisy a rizika kontaminace zemědělské půdy. Proto bylo pozitivním zjištěním, že modifikovaný biochar pojme třetinu množství fosforu obsaženého v běžně používaném zemědělském hnojivu – jednoduchém superfosfátu. Tento fosfor je lépe přístupný rostlinám než struvit, který vzniká spontánně při nakládání s kalem.

Ověřovanou technologií recyklace fosforu pomocí modifikovaného biocharu lze vyrobit dva druhy fosforečných hnojiv: fosforečnan železitý (možnost opakovaného použití filtru) a fosforem nasycený biochar. Pozitivní vlastnosti biocharu na půdní vlastnosti byly shrnuty v předchozím textu. Výsledky tohoto výzkumu dokazují, že navržený způsob recyklace fosforu z odpadních vod lze aplikovat v technologické praxi.

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Article

Modified Biochar—A Tool for Wastewater Treatment

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Abstract: Global deposits of concentrated phosphates, which are a necessary source for the production of phosphate fertilizers, are limited. These reserves keep getting thinner, and every day, large amounts of phosphorus end up in watercourses. In this study, we verified that modified biochar (saturated with $FeCl_3$ solution and then neutralized with NaOH solution) can adsorb significant amounts of phosphorus from wastewater. Moreover, the agrochemical qualities of sludge water from a municipal wastewater treatment plant, struvite, phosphorus-saturated biochar, and iron(III) phosphate from a reused biochar filter were tested in this study. We determined the amount of mobile phosphorus as well as the amount of extractable phosphorus and its five fractions. It was found that modified biochar can hold one-third of the phosphorus amount contained in the commonly used agricultural fertilizer simple superphosphate (1×10^5 g of modified biochar captures up to 2.79×10^3 g of P). Moreover, plants can more easily access phosphorus biochar fractions than struvite, which is formed spontaneously during sludge management. The results of this research prove that the proposed method of recycling phosphorus from wastewater can be applied in technological practice.

Keywords: biochar; fertilizer; iron(III) phosphate; phosphorus; purification; recycling; wastewater

1. Introduction

Phosphorus (P) is the 11th most abundant element in the Earth's surface (reaching approximately 4×10^{18} g of P) and is, therefore, not considered to be geochemically rare [1]. However, the lack of highly concentrated phosphate reserves has been discussed [2] and, from a practical standpoint, can be considered non-renewable [3]. Phosphate deposits are also unevenly distributed worldwide [4]. For example, Morocco accounts for nearly 50% of natural P deposits [5].

About 90% of worldwide fossil phosphates are used for fertilizer production [6]. Mineral fertilizers are used in intensive farming systems worldwide. At the turn of the millennium, about 1×10^4 g P $\cdot$ ha^{-1} was applied annually to agricultural land worldwide. In Europe, however, this value was 2.5×10^4 g P $\cdot$ ha^{-1} $\cdot$ year^{-1} [7]. The total consumption of P fertilizers in the European Union (EU-27) is almost 1.4×10^6 g $\cdot$ year^{-1} [8].

Careless use of phosphorus fertilizers has led to eutrophication problems in developed and large developing countries [9]. A major problem responsible for agrochemicals (including P) escaping from fields is erosion [10]. This also is due to the fact that the efficiency of P fertilizer uptake by plants ranges only from 10 to 25% [11]. Because of this, eutrophication is a global problem causing a decline in the quality of both fresh and marine water worldwide [12]. The continuing high levels of phosphorus leeching into water ecosystems will accelerate harmful processes such as algal blooms or hypoxia in aquatic ecosystems [13], which will lead to significant ecosystem changes and to endangerment of a significant number of species [14]. This is one of the most visible examples of biosphere changes due to human activities [15].

The problems caused by excess phosphorus in the wild are, therefore, unquestionable. On the other hand, phosphorus is a limited element for primary production in agricultural ecosystems [16], and the availability of P in agricultural soils is becoming a global problem [17]. Phosphorus is limited either because it is present in insufficient amounts in soils or in forms that are inaccessible to plants. These factors subsequently lead to a decrease in agricultural production [18].

The P cycle in the soil, and consequently other parts in the environment, is influenced not only by the intensity of sorption processes in the soil but also by the type and form of the phosphorus source, the climate, the microbial activity of the soil, and the plants themselves. Complex edaphic processes lead to P immobilization in soil, hampering its timely and sufficient availability for uptake by plants [19]. P can also accumulate significantly in soil despite the current decline in its plant-accessible forms [20]. Therefore, balancing the complete soil system is the only reliable solution. This also takes into account, in addition to omnidirectional inputs and outputs, P transformations and cycles in the soil [21].

In the P cycle, including mining and processing, there are significant losses through its use and consumption. In the face of P deficiency, it is a challenge to minimize these losses and use P as efficiently as possible [22]. Estimates when reserves of P fossil resources will be depleted vary. For example, Scholz and Wellmer [23] do not think this will happen in the coming decades. Cabeza et al. [24] predicted that global P resources will be depleted in 70–175 years. Cordell and White [1] discussed in detail many aspects of P reserves, mining, and consumption, and they explained why it is almost impossible to accurately predict the depletion of P reserves. However, there is general agreement that depletion will take place sooner or later.

While agriculture is the largest consumer of non-renewable phosphorus sources, it is not the only source of P ending up in water resources. For example, it is known that one person produces about 550 liters of urine per year [25], which contains about 365 g of P [26]. By converting this amount, we find that the wastewater of a city with 100,000 inhabitants contains 150 m^3 of urine per day with 1×10^5 g of pure P. However, a number of products containing P are used in households (for example, washing powders, toothpastes), which also reach the wastewater. Thus, on average, there is approximately 2.3 g of P for one person per day [27]. It is therefore clear that urban wastewater is a source of P that needs to be addressed.

Sludge water is an even richer source of P. It is produced from wastewater during sludge management in urban wastewater treatment plants after anaerobic sludge stabilization. It often contains up to tens of g/L of P, although much lower concentrations are also common (2.5–27.0 $g \times 10^{-3}$ P/L) [28]. Sewage sludge is a seemingly accessible source of P for soil fertilization. However, there is risk of soil contamination; therefore, use of sludge is subject to strict legislation in developed countries. For this reason, farmers have limited interest in the use of sewage sludge for fertilization [29].

Due to the above-mentioned reasons (limited reserves of P resources, eutrophication of water, etc.), it is necessary to recycle P as much as possible. Especially in developed countries, but also in developing countries, the issue of P recovery from wastewater has been given considerable attention. A large number of technologies have already been developed for recycling P, or at least removing it from wastewater. Only some of them are outlined below.

Currently, precipitation of struvite ($MgNH_4PO_4 \cdot 6H_20$) from sludge water after anaerobic sludge stabilization is considered the most promising method. Struvite is formed spontaneously at higher pH or in the presence of Mg^{2+} salts in sludge waters. With this technology, the struvite precipitation efficiency depends mainly on the Mg:NH4:P ratio and the pH of the sludge water. The molar ratio of Mg:P should be 1.3:1 [30] with an optimum pH = 9, but a pH of 8.5 is sufficient [31]. Struvite is also known as a P fertilizer for soil [32,33]. It is a poorly soluble, crystalline substance that slowly releases both P and nitrogen into the soil [34]. However, further examination of whether P recycling technologies, crystallization precipitation technologies, etc., reduce P accessibility are needed.

Crystallization of P is another technology [35]. The process works well mainly at higher P concentrations in sludge water. It crystallizes calcium phosphate with crystallization cores, which are sand, slag, or diatomaceous earth particles in a fluidized bed reactor. The most promising crystallization technology is struvite crystallization.

The recovery of P is also possible using ion exchange. PO_4^{3-} is removed from sludge water by porous P-selective media, exchanging with cations such as Cl^- to produce P-depleted effluent while maintaining charge neutrality in the solid media [36].

Adsorption is another group of technologies. Sorbents with Fe, Ca, and Al are used whose interaction with PO_4^{3-} leads to the formation of hydroxylapatite or vivianite minerals, to ion exchange by surface adsorption or internal ion exchange, or to the creation of hardly definable clusters. The sorbents used are fly ash, Fe oxides, blast furnace slag, and bauxite extraction wastes. Again, these technologies are suitable when there are higher concentrations of P in sludge water and the plant-accessibility of P in the product is low [37].

Phosphorus removal by magnetic microsorbents, such as carbonyl iron particles [38], or Fe_3O_4 nanoparticles embedded in an SiO_2 matrix coated with P-selective ZnFeZr [39] is based on principles similar to adsorption. Magnetic microsorbents are adsorbent materials that have magnetic properties when suspended in wastewater. Nutrients adsorbed on magnetic media are recovered by capturing the suspended media using high-gradient magnetic separators, with subsequent regeneration and precipitation from the regenerant [40].

Other methods used for wastewater treatment include, for example, artificial wetlands [41]. Another method is the biological removal of P using polyphosphate-accumulating bacteria [42]. This microbial process is called enhanced biological phosphorus removal and has, in practice, been incorporated into numerous activated sludge treatment plants [43]. Capturing P with biomass is also promising. Cyanobacteria (*Phormidium bohneri, Rhodobacter capsulatus*), algae (*Chlorella vulgaris*), or algae with macrophytes (*Chlorella vulgaris and Lemna minuskula*) are commonly used.

In the case of phosphorus in terrestrial ecosystems, the total phosphorus in soil is present in a large number of fractions. Most fractions contain P that is in a form not accessible to plants. Forms of P in the soil that have minimal importance in plant nutrition are usually iron phosphates, phosphorus from non-hydrolysable organophosphates, non-extractable (residual) phosphorus, and phosphorus from specific organophosphates (bound in humification products) [44].

Phosphorus from sewage sludge, sludge water, and other forms bound to an easily hydrolysable, and thus degradable, organic matter are easily accessible to plants [45]. Generally, mobile organic and inorganic phosphorus are critical for plants, especially phosphorus in soil solution, microbial biomass, mobile and potentially accessible organic phosphorus, and mobile and potentially accessible inorganic phosphorus. The mobile P fraction (P_{mob}) encompasses P present in anions of water-soluble, inorganic salts and P present in easily mineralizable, organic forms. The extractable P fraction (P_{extr}) denotes the sum of calcium (Ca-P), aluminum (Al-P), and ferric (Fe-P) phosphates [46]. Ca-P can be divided into three categories: CaP-I, CaP-II, and CaP-III. Simply put, a higher Roman numeral indicates a reduced availability of P for plants. Al-P is even less accessible, and Fe-P shows an even worse degree of availability [47].

It is therefore clear from the text above that when considering the source of P as a plant nutrient, the amount of P in the product should be taken into account as well as its form and, hence, accessibility to plants. This research assumes the possibility of using modified biochar as a phosphorus sorbent in wastewater and, subsequently, as an easily accessible source of phosphorus for plants. The aim is to purify wastewater by removing phosphorus and, thus, reduce the amount that enters the environment as well as obtain a high-quality phosphorus fertilizer with high added value.

2. Material and Methods

2.1. Origin and Characteristics of Products 1 and 2

Product 1 was sludge water. Water was taken in September 2018 from the central wastewater treatment plant in Prague (Bubeneč, part of the city) after it passed through a sedimentation tank. Prior to sampling, phosphate precipitation was stopped. The sludge water had a temperature of 16 °C and pH 7.2. The concentration of P was 4.9×10^{-2} g PO_4^{3-}/L, and total phosphorus was 6.2×10^{-2} g P/L.

Struvite (Product 2), which is generated spontaneously in the presence of Mg^{2+} in wastewater treatment plants, was also tested. Struvite precipitation from sludge water was carried out in a six-basin coagulation mixer for 24 h according to the methodology described by Sýkorová et al. [28]. Product 3, phosphorus-saturated biochar, and Product 4, iron(III) phosphate ($[Fe(PO_4)_3]^{6-}$), are newly tested products whose technical development is described below.

2.2. The Essence of the Technical Method to Obtain Products 3 and 4

Recycling sorption technologies have been designed and tested. The sorbent was a biochar filter. Its sorption capacity was saturated with $FeCl_3$ solution (10%), neutralized with NaOH solution (5%), and then washed with water.

After washing the saturated biochar filter with clean water, purified wastewater was pumped through the filter from the sewage treatment plant (the location of the biochar filter in the water purification process is shown in Figure 1). If P-rich sludge water from the treatment plant (after anaerobic sludge stabilization) is to be used, it must be cleared of suspended organic substances via sand filtration, and possibly also by activation, because the organic substances can quickly clog the biochar filter. After reaching the sorption capacity of the filter, it was then possible to select from two methods to use the obtained material.

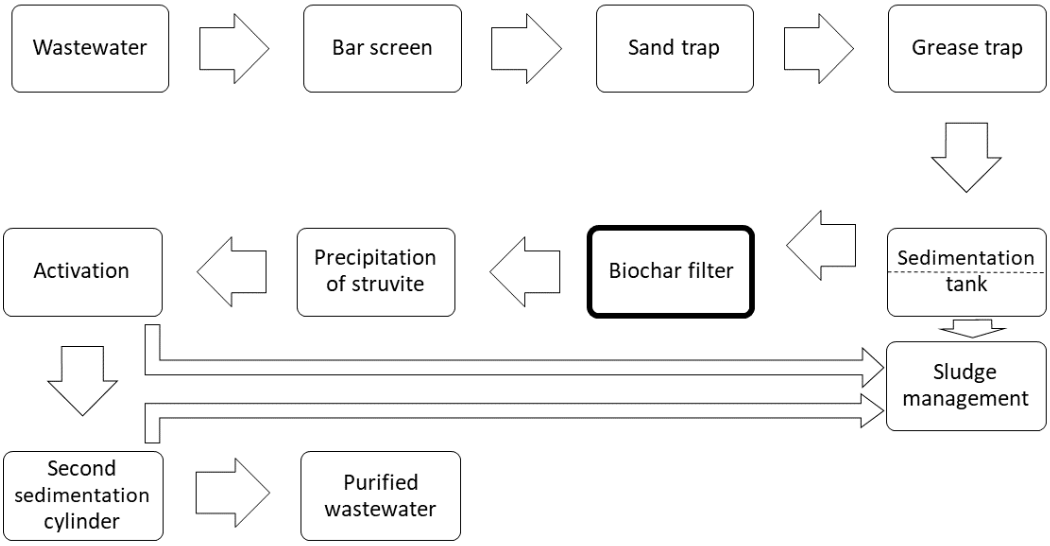

Figure 1. Wastewater management process.

Phosphorus-saturated biochar, Product 3, was ready for use as a P fertilizer after drying.

If the other method is followed, in which the filter is used repeatedly, then Product 4 (iron(III) phosphate) is obtained. The filter was washed with dilute HCl (pH of washing solution = 5.5). The solution was then neutralized with NaOH to pH = 8 to give iron(III) phosphate. The filter was again ready for use after re-saturation with iron.

2.3. Description of the Practical Implementation of Products 3 and 4

In the experiment, 200 g of biochar was used. The biochar was made from coconut shells via carbonization at a temperature of up to 350 °C, then mixing with a 10% $FeCl_3$ solution, and finally leaving at 20 °C for 12 h. After filtration, a 5% NaOH solution was allowed to flow through the wet biochar until the pH at the effluent remained unchanged. This was followed by washing with water until the pH at the effluent remained unchanged. Dry matter was found in the wet product after removing the water.

A phosphate solution was brought to the filter. Concentrations of 0, 20, 40, 60, 80, and 100×10^{-3} g P/L were used. The absorbed amount of P per 1 g of modified biochar and the equilibrium concentration of P in the solution after absorption were determined. A chart was then created in which the absorbed amount ($g \cdot 10^{-3}$ P/g of sorbent) was written on the vertical axis and the concentration of P (g/L of the equilibrium solution) on the horizontal axis. The chart showed how much P the biochar was able to capture. The empirical Freundlich isotherm for phosphorus adsorption was used:

$$q = K_f \times c^{1/n} \tag{1}$$

where q is the sorbed P ($g \cdot 10^{-3}$ P/g of sorbent), K_f is the Freundlich partitioning coefficient, c is the equilibrium P concentration in the supernatant solution ($g \cdot 10^{-3}$ P/L), and $1/n$ is the sorption intensity.

2.4. Evaluation of Fertilizer Product Quality

Consequently, the following fertilizers were used to evaluate the fertilizer efficiency:

1. Original sludge water,
2. Struvite precipitated from sludge water,
3. Phosphorus-saturated biochar, and
4. Iron(III) phosphate from a reused biochar filter.

Due to the low mobility of P in soil, long-term contact of the P source with soil was simulated to assess the agrochemical quality of the obtained fertilizer products.

A sample of Haplic Cambisol (Table 1) soil was saturated with water to maximum capillary capacity, released from the Kopecký cylinder, and crushed and combined with the investigated P source in a 1 L polyethylene bottle. To obtain measurable results, a higher total P addition was chosen (the same for all four phosphorous sources), namely 6.2×10^{-3} g P per 1 g of soil. Thus, the sludge water had to be concentrated by evaporation in a water bath to one tenth of the volume. The bottle was sealed and shaken on a rotary shaker for 24 h. Afterwards, it was stored in a thermostat at 28 °C for 3 days. After removal from the thermostat, the bottle was emptied into a flat photographic dish, aerated, returned to the polyethylene bottle, and the evaporated water was added. This procedure was repeated 5 times.

Table 1. Phosphorus in Haplic Cambisol soil before the experiment (± SD; Mehlich II).

P_{mob} ($g \cdot 10^{-3}$ /$g \cdot 10^3$)	P_{extr} ($g \cdot 10^{-3}$ /$g \cdot 10^3$)	CaP I (%P_{extr})	CaP II (%P_{extr})	CaP III (%P_{extr})	AlP (%P_{extr})	FeP (%P_{extr})	P_{org} ($g \cdot 10^{-3}$ /$g \cdot 10^3$)	P_{tot} ($g \cdot 10^{-3}$ /$g \cdot 10^3$)
25 ± 4	138 ± 17	10	14	22	26	28	294 ± 23	1828 ± 22

Upon completion of preparing the experimental soil, the mobile phosphorus as well as extractable soil phosphorus and its five fractions (CaP-I, CaP-II, and CaP-III fractions, which are easily accessible to plants, and Al-P and Fe-P) were determined. Pmob was analyzed according Kovar and Piezinsky [48]. P_{extr} was analyzed according to Ginzburg and Lebedeva [49]. Following this procedure, 1 g of soil was extracted successively with 1% $(NH_4)_2SO_4$ (pH 4.8), 0.5 N CH_3COOH (pH 4.2), 0.5 N NH_4F (pH 8.5), 0.1 N NaOH, and 0.5 N H_2SO_4. Fractionation of organic P was not performed in this experiment.

Data were analyzed using STATISTICA (version 12, TIBCO Software Inc., Palo Alto, CA 94304 USA). One-way analysis of variance (ANOVA) with a subsequent post hoc Tukey test was used to analyze differences between P sources. The level of significance for all analyses was $\rho \leq 0.05$.

3. Results and Discussion

3.1. *Efficiency of Sorption*

This study of recycling phosphorus from wastewater using biochar brought attention-grabbing results. From Figure 2, it can be seen that the capacity of the modified biochar was 27.93 mg of P $\cdot$ g^{-1} of sorbent. In other words, 1 g of given biochar (in the described treatment) at the maximum test concentration of the original solution (100 g × 10^{-3} P/L) was able to capture 27.93 × 10^{-3} g of P (with a sorption efficiency of 27.9%), i.e., 6.4 × 10^3 g of P_2O_5. For comparison, the classic, simple superphosphate P fertilizer contains about 16 % P_2O_5.

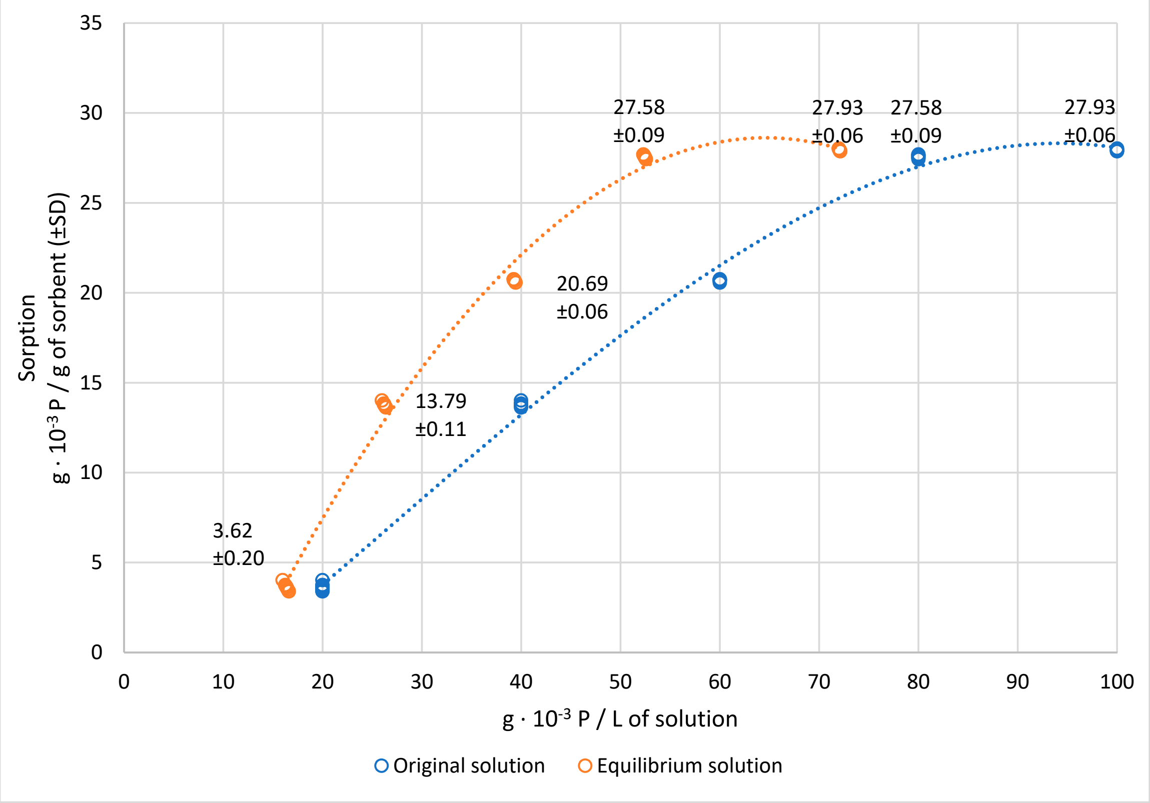

Figure 2. Adsorbed amount of phosphorus at different concentrations of solution.

However, a higher sorption efficiency was recorded in concentrations of 40–80 g $\cdot$ 10^{-3} P/L, and a maximum of 34.5% P was purified from the wastewater. Nonetheless, the amount of adsorbed phosphorus was lower. If there was only 20 × 10^{-3} g P/L in the wastewater, 1 g of biochar would only capture 3.6 × 10^{-2} g of P. The P content in the wastewater was reduced by less than one fifth (from 20 × 10^{-3} g P/L to 16.4 × 10^{-3} g P/L).

The Freundlich equation, which gives an expression that defines the surface heterogeneity and the exponential distribution of active sites and their energies, has the form $q = 8.625 \times c^{1/0.735}$, where the coefficient of determination (R2) is 0.86. In this context, it should be noted that the sorption properties of different biochars may be quite different depending on the type of pyrolysed organic matter or the temperature during the process [50].

Compared to technologies that employ struvite precipitation, sorption by a biochar filter appears to be less effective. The efficiency of P removal from wastewater by struvite precipitation is mentioned in the literature to be more than 90% [51]. For this reason, struvite precipitation should not be neglected in the wastewater treatment process, but instead placed behind the biochar filter.

3.2. Quality of Products

Four products were obtained from sludge management, which can be used as phosphorus fertilizers, and were analyzed. Differences in phosphorus content between various fractions (Figure 3) were found (one-way ANOVA, $F_{(9, 34.223)} = 34{,}153$, $p < 0.0001$).

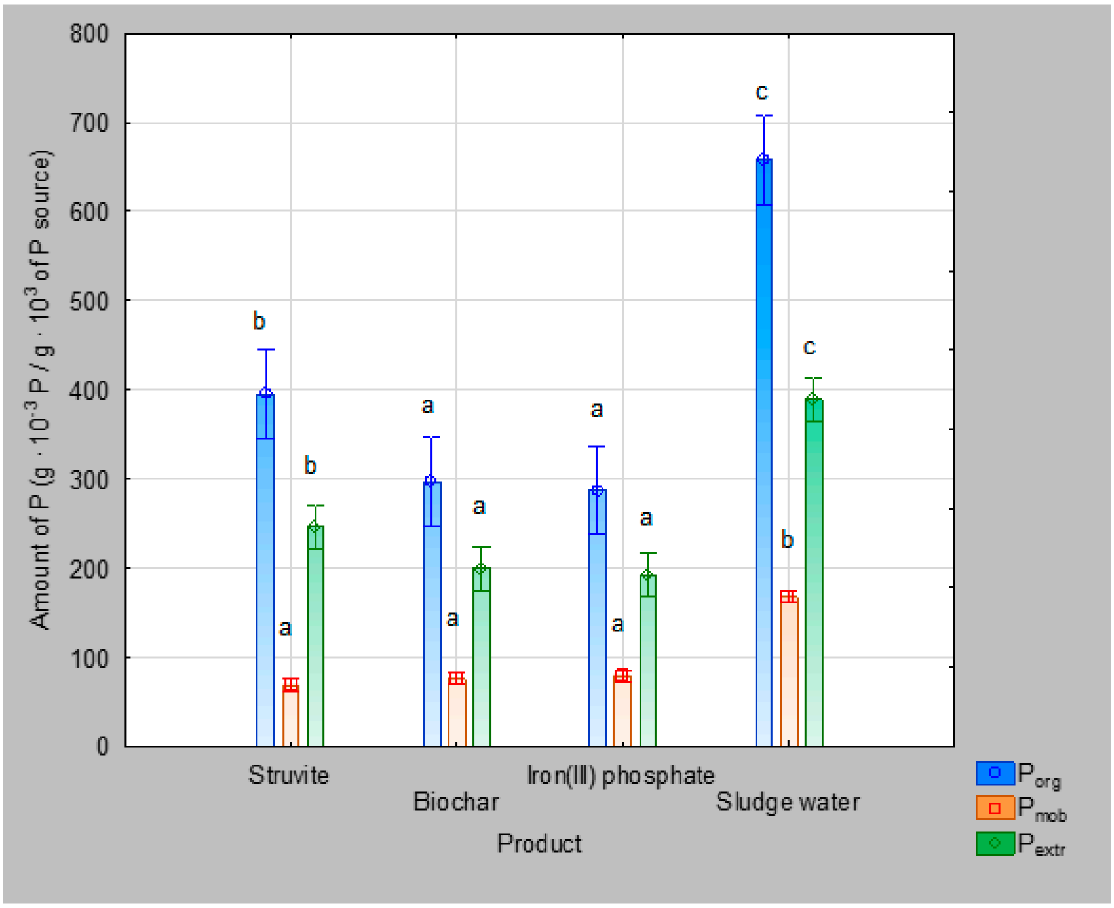

Figure 3. Phosphorus in Haplic Cambisol soil after addition of 6.2×10^{-3} g of P (in phosphorus source)/g of soil (Mehlich II). Vertical bars denote 0.95 confidence intervals. Significant differences between the concentrations of different kinds of phosphorus among the tested extraction products are shown in small letters (Tukey's honest significance test).

The experiment proved that the original sludge water contained the highest amount of total phosphorus, including the P_{mob} fraction, which is crucial for plant nutrition. The P_{org} content was also the highest in sludge water, followed by struvite. In the biochar and iron (III) phosphate products, the amount of P_{org} was the lowest. The same order of values of phosphorus content was found in the P_{extr} fraction.

From the above, it seems that the application of sludge water to soil would be the most beneficial from a plant nutrition standpoint. However, the disadvantage of using sludge water is its high transport costs caused by the high water content [52]. Wider use of water sludge has also been hampered by strict legislative rules [53]. This is because sludge can contain harmful organic and inorganic contaminants, and in some cases the application of sludge to agricultural land can contaminate water, soil, and the food chain [54].

If we do not take into account wastewater, struvite contained the most P and may appear to be the best fertilizing product at first glance. It is also often rated as an excellent, slowly soluble P fertilizer in the literature [32,55,56]. However, from an agricultural point of view, the agrochemical quality of the obtained phosphorus sources is essential. Phosphorus is extremely immobile in soil [57], and its losses by washout from the soil are negligible. Moreover, the amount of P in agricultural soils is still relatively small compared to what plants need in terrestrial agroecosystems [58]. The assumption that low solubility of P fertilizers is an advantage for fertilization and plant nutrition is, therefore, not justified. As many accessible forms of phosphorus as possible are required in agricultural practice. The quality of struvite as a P fertilizer and its solubility were covered in Degryse et al. [59]. They assumed that struvite is considered by many authors to be a quality P fertilizer, as their results are based on experiments where struvite was mixed directly into soil in powder form. Nevertheless, in agricultural practice, struvite must be applied to fields in the form of granules. However, this form of struvite greatly reduces its solubility. Solubility is also significantly influenced by the soil pH. Intensive biological activity also plays an important role in this context [60,61]. Thus, struvite as a phosphorus fertilizer is not optimal.

The distribution of P_{extr} into fractions according to plant accessibility is shown in Figure 4. From the point of view of plant accessibility, the most important fractions were CaP-I and CaP-II. As far as these fractions are concerned, better results were found for products based on the use of biochar in comparison to struvite. Furthermore, both biochar-based products have fewer plant-inaccessible CaP-III fractions than struvite. If we compare phosphorus-saturated biochar and iron(III) phosphate from an agrochemical point of view, phosphorus-saturated biochar seemed to be slightly better. In addition, biochar itself has a number of properties that improve the soil [62,63]. The influence of biochar on the increase in soil water retention capacity [64] in support of biological activity [65] was described. Biochar is also important for climate protection because it can sequester carbon [66]. Compared to struvite, both biochar-based products have fewer plant-inaccessible CaP-III fractions.

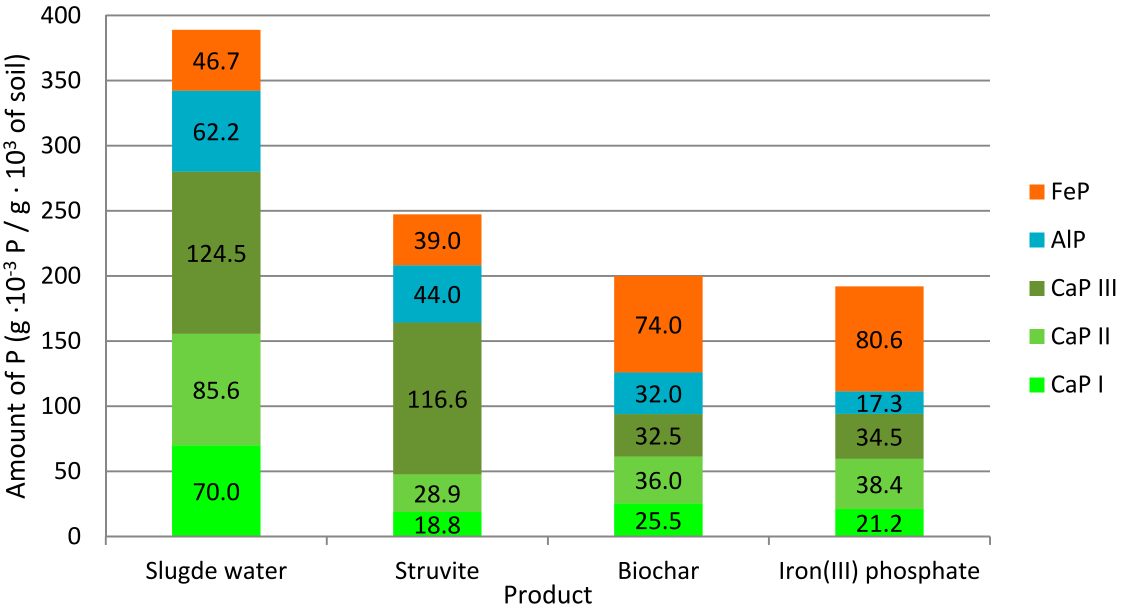

Figure 4. Fractionation of P_{extr} into categories.

The price of biochar is the main factor to consider, from an economic perspective, when implementing this technology. However, these costs can vary greatly over time, location, and input materials. Data on the price of biochar in specialized literature are different. According to Jirka and Tomlinson [67], the global mean price of 1 × 10^3 g of biochar is 2.65 USD. Vochozka et al. [68] report 0.3–0.5 EUR per 1 × 10^3 g. Latawiec et al. [69] claim that the potential benefits of its use outweigh the great labor cost, and as a result biochar is 617% more expensive than common fertilizers. Nonetheless, biochar should not be valued via conventional nutrient optics (as fertilizer), nor as a biofuel. It should be priced, rather, for its soil-improving properties [70]. On the other hand, smaller-scale biochar production near feedstock sources and/or application sites that incorporate energy recovery can further reduce production costs, reaching close to zero. In addition, biochar cost could be further reduced when combined with other new technologies, for example novel thermosiphon-powered reverse osmosis [71] or solar thermal heating applications [72]. Therefore, its use and importance has increased in recent years [73]. Given the additional benefits from biochar use, such as carbon sequestration, farmers could also benefit from eventual payments for ecosystem services to leverage the costs and contribute to global goals to combat climate change [69].

4. Conclusions

The presumption that, from an agrochemical point of view, sludge water would be the best source of phosphorus for agricultural crops was confirmed (it contained the most phosphorus in all fractions). Nevertheless, its use in many countries is hindered by legal regulations. Therefore, other possibilities of using wastewater as a source of fertilizer for plants were investigated. We found that biochar can be successfully used in the wastewater treatment process as a phosphorus sorbent. Modified biochar in the amount of 1 × 10^5 g can capture 2.79 × 10^3 g of P. With this method of recycling, two types of products (phosphorous fertilizers) can be produced: iron(III) phosphate (possibility of repeated filter use) and phosphorus-saturated biochar. In addition to phosphorus, the latter product also supplies biochar to the soil, which is widely recognized to improve soil. Phosphorus-saturated biochar and iron(III) phosphate had good fertilizing properties; they contained a total of 61.5 and 59.6 $g \times 10^{-3}$ P/g · 10^3 of soil, respectively, in easily accessible fractions CaP-I and CaP-II. Struvite, which is created spontaneously in wastewater treatment plants, contained only 47.7 $g \times 10^{-3}$ P/g · 10^3 of soil in easily accessible fractions. It contained an especially low accessible CaP-III fraction (116.6 $g \times 10^{-3}$ P/g · 10^3 of soil). Such fractions may be a source of P nutrients in the long-term, but they are unsuitable as an accessible fertilizer.

Highlights

- Retrieval of phosphorus from wastewater by a biochar filter
- Obtaining a soil improver containing easily plant-accessible phosphorus
- The technology has the potential for use in waste management and agriculture

Author Contributions: Conceptualization, M.K. and L.K.; methodology, L.K.; formal analysis, O.S.; investigation, F.T., J.P., R.V., J.B. and F.F.; resources, X.X.; data curation, O.S.; writing—original draft preparation, M.K. and L.K.; writing—review and editing, M.K and P.M.; supervision, D.B.; project administration, P.B.; funding acquisition, P.K. All authors have read and agreed to the published version of the manuscript.

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6 Závěr

Půdní organická hmota je nezastupitelnou složkou všech zemědělských půd. Půdy bohaté na kvalitní organickou hmotu jsou kypré, snadno se zpracovávají, dobře hospodaří s vodou i živinami a díky tmavší barvě se i rychleji prohřívají. O jejím významu pro půdní úrodnost nemůže být pochyb. Ne každá látka organického původu ale musí být nutně přínosem pro kvalitu půd. Nejen mezi potenciálními zdroji organické hmoty, ale i organickou hmotou v půdě, jsou značné rozdíly.

Pro činnost půdních mikroorganismů je nutný kvalitní zdroj energie. Tím jsou zejména labilní frakce půdní organické hmoty, které zároveň slouží jako citlivé ukazatele změn kvality organické hmoty. Vhodnými indikátory jejích přeměn, jež jsou vyvolávány různými typy hospodaření, jsou obsahy vodou extrahovatelného organického dusíku a uhlíku a obsah dusíku v partikulární organické hmotě.

V úrodné půdě však musejí být zastoupeny i frakce poněkud stabilní, které mohou díky svým vlastnostem zvyšovat půdní úrodnost prostřednictvím své kationtové výměnné kapacity nebo díky pozitivnímu vlivu na půdní strukturu. Nejstabilnější organické látky pak mohou dlouhodobě ukládat uhlík do půdy a snižovat tak jeho koncentraci v atmosféře. Je proto žádoucí zvýšit zásoby jak labilních, tak i stabilních forem organické hmoty v půdě. V této práci byla představena jednoduchá laboratorní metoda, kterou lze v půdním vzorku kvantifikovat množství frakcí relativně labilních a relativně stabilních. Má-li být organická hmota považována za prostředek pro sekvestraci uhlíku, musí být specifikován časový horizont, po který se s uložením uhlíku do půdy uvažuje.

Poměrně novým fenoménem je využití biocharu v zemědělství. Dříve se v odborných publikacích objevovaly nekritické názory popisující biochar jako ideální půdní zlepšovač. S rostoucím počtem provedených výzkumů se ale charakter zveřejňovaných textů začal měnit. Je vždy nutné brát v potaz specifické vlastnosti určitého biocharu a odpovědi dané půdy na jeho přítomnost. Vlastnosti biocharu se mohou zásadně lišit v závislosti na vstupním materiálu, podmínkách pyrolýzního procesu i případné následné úpravě. Tato práce může na základě několika provedených pokusů pozitivní účinky konkrétních biocharů na půdní úrodnost potvrdit. Aby mohl být vliv biocharu na půdu a její úrodnost detailně objasněn a popsán, je nezbytné provést řadu dalších laboratorních i terénních výzkumů. Zásadní otázkou, která v této práci řešena nebyla, zůstává ekonomická stránka výroby a využití biocharu v zemědělské praxi.

„There is no such thing as a post-agricultural society“ (Holmberg et al., 1991).

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Seznam použitých zkratek

Půdní organická hmota – POH

Primární půdní organická hmota – PPOH

Kationtová výměnná kapacita – KVK

Historický black carbon – HBC

Antropogenní black carbon – ABC