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Amending solid carbon from methane cracking to arable soils: A sustainable approach to increase carbon storage and heavy metal immobilization?

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Abstract. Carbon dioxide emissions from burning fossil fuels play a major role in driving global climate change. Reducing these emissions through innovative technologies is critical to achieve climate change mitigation goals. Methane pyrolysis, including catalytic and "plasmalytic" approaches, has attracted attention for its ability to produce so-called turquoise hydrogen alongside solid carbon as a by-product that could be reused as soil amendment. This study investigated the potential of solid carbon materials from catalytic pyrolysis and plasmalysis, alongside reference materials (biochar and graphite), to improve soil hydraulic properties and to reduce heavy metal mobility and whether ecotoxicological reactions affect soil organisms. In experiment 1, two arable soils of contrasting textures (sand and silty loam) were amended with these carbon materials at an application rate of 40 t ha^{-1}, followed by assessments of soil physical properties, soil respiration rate, microbial biomass, extractable organic carbon, nitrogen mineralization, the activity of soil macro- (earthworms) and mesofauna (springtails, *Folsomia candida*). In Experiment 2, we evaluated heavy metal mobility and availability in metal-contaminated soils. In uncontaminated soil, solid carbon from plasmalysis (SC_{plas}) increased water retention of the silty loam, particularly in the range of pF 1.8–3.0, but had no effect in the sandy soil, likely due to its hydrophobic properties, which limited moisture retention. In the silty loam, SC_{plas} reduced microbial activity and the abundance of springtails. In the sandy soil, it had a negative effect on soil macrofauna (earthworms). The solid carbon from catalytic pyrolysis (SC_{cat}) had almost no effect on the biological properties studied. In soils contaminated with heavy metals, SC_{plas} showed strong immobilisation of heavy metals particularly for Cd and Cu, across several sites, outperforming the reference materials. However, SC_{cat} increased Cd mobility at some sites, indicating little or even adverse effects on heavy metal mobility. Our results highlight the promise of SC_{plas} for site-specific soil improvement, while cautioning against its hydrophobic effects in sandy soils. In contrast, SC_{cat} has more negative effects, especially ecotoxicological than positive ones depending on soil.

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1 Introduction

Greenhouse gas (GHG) emissions, in particular carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O), considerably contribute to global climate change (Chidi et al., 2021; Filonchyk et al., 2024; Malhi et al., 2020). Reducing GHG emissions is crucial to achieve the targets outlined in the European Climate Change Action Plan (European Commission, Directorate-General for Energy, 2020) and to mitigate climate change impacts as envisioned in the IPCC scenarios for limiting global warming to 1.5°C or 2°C (Rogelj et al., 2018). Negative emissions technologies, such as Bioenergy with Carbon Capture and Storage (BECCS), have emerged as key strategies to achieve these targets (Jones and Albanito, 2020). The production of biogas is one important renewable energy source in Europe. The conventional use of biogas includes releasing CO_2 and does not lead to negative emissions (Shahbaz et al., 2021). To address this limitation, hydrogen production from biogas has gained attention, particularly turquoise hydrogen, which is, by definition, hydrogen produced by methane pyrolysis. This method yields solid carbon as a by-product, which can be stored or repurposed (L'hospital et al., 2024; Radoiu and Mello, 2024; Tong et al., 2023).

Two prominent methane pyrolysis approaches, plasma and catalytic pyrolysis, offer promising pathways to generate hydrogen and solid carbon. While plasma pyrolysis is energy-intensive, catalytic pyrolysis using microwave technology is more energy-efficient (Kappe, 2004). In addition to its efficiency, microwave-assisted catalytic pyrolysis shall allow reduced equipment size and environmental impacts (Kappe, 2004; Shen et al., 2014). Both technologies offer the possibility of carbon sequestration if the resulting solid carbon materials are used or stored appropriately.

An attractive possibility for storage of solid carbon materials is the amendment to arable soils. The fertility of soils is known to be positively related to carbon content (Farooqi et al., 2021; Giandon, 2015). However, neither the suitability nor the safety of these carbon materials as soil amendments have been investigated so far. Nothing is known about potentially positive or negative side effects on soil organisms and soil functions and properties. One may expect that the solid carbon materials from biogas conversion behave like biochar, the product of biomass pyrolysis. Biochar has been extensively studied as a soil amendment. With its high specific surface area and porosity, it improves soil aeration, reduces bulk density, and enhances water infiltration (Edeh et al., 2020). It can also stabilize soil aggregates, strengthening soil structure and reducing erosion (Godlewska et al., 2021). Further, biochar can support microbial communities by providing a porous habitat that offers physical protection and stable conditions. Its surface properties also facilitate the sorption of organic compounds, which can affect microbial access to nutrients and contaminants (Ahmad et al., 2014; Gul et al., 2015; Zhu et al., 2017). It increases carbon sequestration, reduces greenhouse gas emissions, and positively influences both soil nitrogen (N) dynamics (Anand et al., 2022; Clough et al., 2013). Additionally, biochar can lower metal mobility through precipitation or sorption processes, thus reducing metal concentrations in the soil solution (Gholizadeh and Hu, 2021; Majewska and Hanaka, 2025). It is, however, noteworthy that biochar properties vary greatly with feedstock, pyrolysis conditions, and post-production treatments (Faloye et al., 2024). For example, higher pyrolysis temperatures typically produce biochar with greater specific surface area and alkalinity, leading to stronger nutrient retention and water-holding capacity (Brewer et al., 2009). Therefore, assessing effectiveness and safety of carbon-based amendments, in particular those from other origins, requires targeted research.

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Building on the well-documented benefits of biochar, we hypothesize that the novel carbon materials may exert beneficial or favorable influences on soil organisms, soil functions and properties. We investigate the potential of two solid carbon materials produced in the framework of the EU-Project TITAN, which specifically explores pathways to generate hydrogen without CO_2 emissions while capturing and storing carbon in solid form (https://titan.cnrs.fr/). Specifically, the study focuses on (i) the ability of the solid carbon materials to modify soil hydraulic properties, including water retention and conductivity, (ii) their ecotoxicological effects on soil microorganisms, meso- and macrofauna, and associated soil functions; and (iii) their impact on the mobility and bioavailability of heavy metals.
The two novel solid carbon materials (produced through direct plasma or catalytic pyrolysis of methane) were tested across two arable soils with contrasting textures (sand and silty loam) and compared with established references, biochar and graphite. Soil physical properties, including water retention and hydraulic conductivity, were assessed using the evaporation method and pressure plate apparatus. We further assessed ecotoxicological impacts on soil microorganisms and microbially associated soil functions, springtails and earthworms. By different extraction methods ($CaCl_2$, EDTA, and ammonium nitrate) we evaluated the mobility and bioavailability of heavy metals. Our findings provide information, whether and under what circumstances solid carbon from plasma and catalytic pyrolysis can be recommended as an amendment to agricultural soils.

2 Material and Methods

2.1 Solid carbon and reference materials

Solid carbon materials were synthesized from pure methane by two different methods, by catalytic pyrolysis (TITAN project) (L'hospital et al., 2024) and plasma pyrolysis. Solid carbon from catalytic pyrolysis (SC_{cat}) was formed using a quartz fluidized bed reactor filled with Fe@carbon catalyst, which was heated by an electric furnace (TSVH 12/40/305, Elite Thermal Systems Limited, Merket Horborough, United Kingdom) under methane flow (L'hospital et al., 2024). After the reaction, the catalytic bed was recovered from the reactor and the obtained carbon deposit isolated from the iron metallic part of the catalyst using a mixture of $HCl:HNO_3$ (3:1) while gentle stirring (250 rpm) for 4 hours at 50°C. The carbonaceous deposit was filtered and then washed with demineralized water until a filtrate with pH 7 was obtained. The filtered deposit was then dried overnight at 150°C.
Solid carbon from plasma pyrolysis (SC_{plas}) was obtained from a microwave reactor within which a methane plasma was created, which resulted in the formation of mainly solid carbon and hydrogen. The SC_{plas} was washed with dichloromethane to extract any residual PAHs that may have formed during plasma formation with methane (Ortega et al., 2021).
Biochar and graphite were chosen as reference materials. The biochar was produced from *Miscanthus x giganteus* residues that were processed at a pyrolysis temperature of 850°C in a low oxygen environment for 30 min (Pyreg, Dörth, Germany). The graphite (Pyrolytic Graphite Powder) was ordered from ACS Material (Pasadena, USA). The characteristics of the studied materials are shown in Table 1.

Table 1. Characteristics of the studied solid carbon materials

	Solid carbon from catalytic pyrolysis (SC_{cat})	Solid carbon from plasma pyrolysis (SC_{plas})	Biochar	Graphite
Starting material	methane	methane	Straw (*Miscanthus x giganteus*)	graphite
Structure	crystallized	crystallized	amorphous	crystallized
Specific surface area, (m^2 g^{-1})	5.9	58.8	346.4	17.4
Mesoporosity	2< pore diameter <50 nm	n.d.	2< pore diameter <50 nm	2< pore diameter <50 nm
Particles size	< 200 µm	<200 µm	125 and 1000 µm	< 50 µm
Metallic iron	1.7 wt.%	n.d.	n.d.	n.d.

n.d.: not determined

2.2 Experimental setup

The study is split into two parts. In either case, the two solid carbon and the reference materials were mixed into the two soils (see below) at a rate of 40 tons ha^{-1}. This application rate was selected based on previous experiments with biochar (Chan et al., 2007; Faloye et al., 2024; Spokas et al., 2009). In Experiment 1, we investigated soil hydraulic properties and ecotoxicological effects of two uncontaminated arable topsoils. In Experiment 2, we investigated the mobility of heavy metals in five arable topsoils that had been exposed to heavy metal inputs over extended periods of time.

2.2.1 Experiment 1 (Soil hydraulic properties and ecotoxicological assessment of uncontaminated arable topsoils)

Soil samples were collected in May 2023 from the top 30 cm of two agricultural field sites, both located in Baden-Württemberg, Germany. Soil textures were sandy and silty loam, respectively. The sandy soil was obtained from Eckartsweier field research station (University of Hohenheim), near Willstätt in the Upper Rhine Valley (48°31'45.12" N, 7°51'18" E). Soil type is a Pseudogley formed from sandy river deposits. The silty loam was obtained from Heidfeldhof field research station (University of Hohenheim), near Stuttgart (53°41'35.88" N, 12°55'23.73" E). The soil type is a stagnant Luvisol derived from loess.

The soil samples were air-dried and passed through a 2-mm sieve before analysis. Prior to the experiment, the soils were characterized to determine their initial properties (Table 2). The soil organic matter content was assessed by loss on ignition (DIN 18128:2002-12, 2002). Soil pH was assessed in 0.01 M $CaCl_2$ solution following the (DIN ISO

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10390:1997-05, 1997) standard. Soil texture was determined by the sieving and sedimentation method (ISO 11277:1998, 1998; ISO 11277:2020, n.d.).

Table 2. Properties of the two soils used in Experiment 1

	C_{org}	N_t	C/N	pH	Sand	Silt	Clay
	(%)	(%)	ratio	($CaCl_2$)	(%)	(%)	(%)
Sandy soil	1.15	0.08	14.4	5.1	64	28	8
Silty loam soil	1.21	0.13	9.3	6.9	9	69	22

The following five treatments were set up with both soils: 1) control (soils without any amendments), 2) with solid carbon from catalytic pyrolysis, 3) with solid carbon from plasmalysis, 4) with biochar and 5) with graphite.

Soil water retention and hydraulic conductivity were simultaneously determined with the simplified evaporation method (Peters and Durner, 2008; Schindler et al., 2010) using the HYPROP device (METER Group, AG, Germany). The hydraulic conductivity measurements were evaluated with the LABROS SoilView-Analysis software (Elrick et al., 1989). To achieve a homogeneous distribution of the materials in soil, soils were thoroughly mixed after amendment and then packed into stainless steel cylinders (250 cm^3 volume) at a target bulk density of 1.3 g cm^{-3} (Lewis and Sjöstrom, 2010; Nakhli et al., 2021).

The volumetric water contents of disturbed soils at permanent wilting point (pF 4.2) were determined using a pressure plate apparatus. Each treatment was replicated four times. The volumetric water contents of all treatments were calculated by multiplying the gravimetric mass recordings by the soil bulk density (1.3 g cm^{-3}).

Plant-available water in the plowing horizon was calculated from the volumetric water content at field capacity (pF 1.8) and permanent wilting point (pF 4.2), assuming a thickness of 0.3 m. This assumption was applied uniformly to both sandy and silty loam soils to standardize comparisons across treatments. Porosity (ϕ, %) was calculated based on the relationship between bulk density (ρ_b, g cm^{-3}) and particle density (ρ_p, g cm^{-3}):

$$\emptyset = \left(1 - \rho_b/\rho_p\right) \times 100, \tag{1}$$

Bulk density was 1.3 g cm^{-3} (assumed constant for all treatments) and particle density assumed to be 2.65 g cm^{-3} (a typical value for mineral soils). This resulted in a porosity of 50.9%.

Air capacity is defined as the difference between porosity *(*ϕ*, %)* and volumetric water content at field capacity (pF 1.8) (Θ_{FC}, %):

$$AC = \emptyset - \theta_{FC}, \tag{2}$$

Air capacity represents the proportion of pore space filled with air in static equilibrium.

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Glass microcosms (500 ml Weck jars, Weckglaeser.com) with an airtight lid were used to study soil respiration, microbial biomass, extractable organic C (EOC) and N mineralization. The five treatments were replicated four times, resulting in a set of 40 microcosms. Each microcosm contained 115 g of fresh soil, equivalent to 100 g of dry mass (DM). 1.11 g of solid carbon or reference materials were mixed into 100 g of dry soil. The amended soil (or control) was then split into four 50 ml Falcon vials (28.75 g fresh weight in the case of sandy soil and 31.25 g fresh weight in the case of silty loam soil). At each of the four sampling dates (7, 14, 35, 56 days) one vial was removed from each microcosm for measurement of microbial biomass, EOC and N mineralization.

Soil respiration was determined according to DIN EN (ISO 16072:2002, 2011) by continuously measuring CO_2 production in the microcosms via CO_2 traps at day 2, 7, 10, 14, 17, 21, 31, 35, 42, 49 and 56 of the incubation. Cumulative CO_2 production was calculated by summing up the CO_2 produced during the intervals. Results are given in mg CO_2 g^{-1} dry mass (DM).

Soil microbial biomass C (C_{mic}) was quantified by substrate-induced respiration (SIR) using a respiration measurement system consisting of 30 measuring units (15 per water bath). Each of these measuring units consisted of a box with a pressure sensor on which a reference chamber and a sample chamber, connected to an electrode chamber, were connected. The sample chamber consisted of two parts, the upper part with the soda vessel (300 µl of 2 M NaOH) and the lower part with the sample vessel (4 g soil fresh weight and glucose (4 mg glucose g^{-1} soil)). The measurement lasted between 48 and 72 hours. Results were expressed as µg C_{mic} g^{-1} soil DM.

The EOC content in soil was determined by extracting 5 g of fresh soil with 20 ml 0.5 M K_2SO_4 on a horizontal shaker at 250 min^{-1} for 30 min. The resulting suspensions were centrifuged at 4070 g for 30 min. EOC in supernatants was measured using a TOC/TN-analyzer (Multi N/C 2100S, Analytik Jena, Germany) and expressed as µg EOC g^{-1} soil DM.

Nitrogen mineralization during the 56 days of incubation was determined by measuring ammonium and nitrate in the same extracts used for EOC quantification using a continuous flow analyzer (Bran + Luebbe Autoanalyzer 3, SEAL Analytical, Hamburg, Germany). Results were expressed as NO_3^--N and NH_4^+-N in µg N g^{-1}soil DM.

For the ecotoxicological study, we used juvenile endogeic earthworms (175-357 mg living biomass) that were collected from the sites where the soils were taken from. Earthworms were kept in these soils before specimens were taken out washed with tap water and were kept in a glass petri dishes with wet filter papers for 24 hours to clean the intestinal contents before the experiment start. The avoidance test was carried out in two-dimensional planar vessels (Fig. 1).

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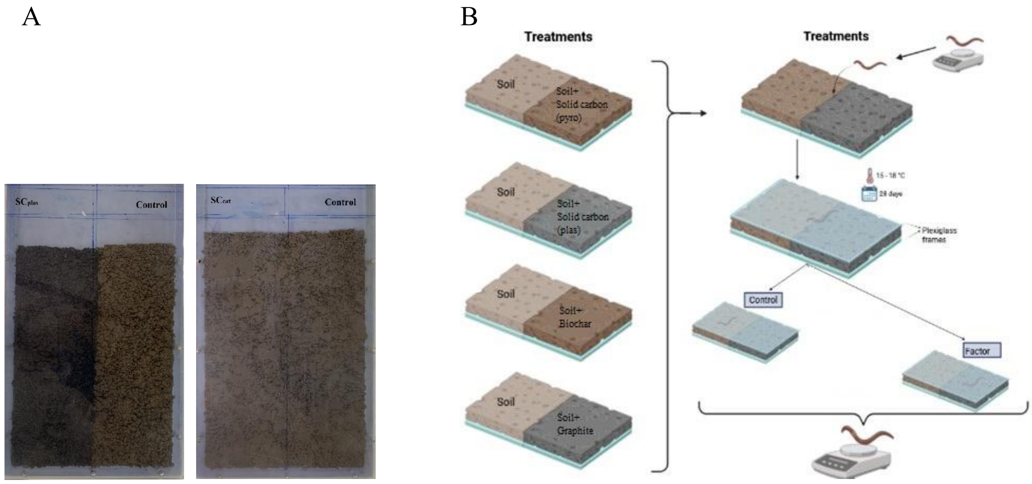

Figure 1. Planar vessel test unit (A) and workflow of the avoidance test (B) with endogeic earthworms

These planar vessels consisted of two perspex PVC sheets (35.3 cm × 18.9 cm) with spacers with spacer strips that create an inner space of 0.3 cm width. To each vertical half of the planar vessels control soil (150 g) and soil amended with one of the four materials (150 g) were placed without any barrier in between. Seven replicates were prepared for each treatment, resulting in a total of 28 planar vessels. Smaller and larger earthworm specimens were evenly distributed among the four treatments. At the experiment's start, one earthworm was placed in each vessel between the control and test soils, allowing it to move freely between the soils. The activity of the earthworm was monitored daily and its position in each half of the vessel was recorded. The test was conducted in the dark (17 °C ± 2 °C) for 28 days, after which the avoidance rate was calculated using the following equation (Han et al., 2021):

$$AR = (N_c - N_t)/N_o \times 100, \tag{3}$$

where AR is the avoidance rate (in %), N_c is the counts how often earthworms were observed in the control soil, N_t is the counts how often earthworms were observed in the treated soil, and No is the total counts per vessel. For instance, an AR of zero percent indicates that the earthworms spent an equal amount of time in the treated soil as in the control soil. As in (Han et al., 2021), results were considered statistically insignificant if the AR did not exceed 25% (ISO 17512-1:2008, 2008).

Springtails (*Folsomia candida*) were cultured in transparent plastic boxes. The boxes were kept in the dark to avoid stress caused by light. The organisms were fed with dried baker's yeast (*Saccharomyces cerevisiae*) once a week. The avoidance test with springtails was carried out in accordance with OECD guideline 232 (OECD, 2009) in plastic boxes (10.3 × 8.5 × 4.1 cm (height × length × depth). Boxes were filled with 100 g of control soil in one half and 100 g of test soil (1.11 g of solid carbon + 100 g of dry soil) in the other half without a barrier in between. Five replicates were prepared for each treatment. At the beginning of the test, 2 mg of dry yeast was homogeneously added to the soil surface in each test box, and then 20 springtails were added. The boxes were closed with lids ensuring gas exchange and incubated at 20 ± 1 °C. Two days later, the animals in each half of the boxes were counted manually under a microscope. Avoidance was calculated using the formula:

$$AR = (N_c - N_t)/N_o \times 100, \tag{4}$$

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where AR is the avoidance rate (in %), Nc is the number of *F. candida* in the control part of the soil, N_t is the number of *F. candida* in the tested part of the soil, and No is the total number of *F. candida* in the box (20 specimens). The results were considered statistically insignificant if the avoidance rate did not exceed 25% (OECD, 2009).

2.2.2 Experiment 2 (Mobility and bioavailability of heavy metals)

For experiment 2 five soils from four sites were taken. Soil samples were collected from the lower terrace of the Oker River, about 16 km northwest of Braunschweig. This area has been subject to wastewater irrigation since 1957. Initial heavy metal assessments in the early 1980s indicated up to 200 grams of cadmium (Cd) input per year, leading to considerable soil contamination. Two separate soil samples, which were sampled in the frame of the study of (Ingwersen, 2001) were used in the present study and referred to Braunschweig 1 and Braunschweig 2.

The second sampling location was near Gundelsheim, adjacent to the Neckar River (49° 17′ 7.15″ N; 9° 9′ 39.4″ E). This site features carbonate-containing brown floodplain soil characterized by silty clay and is frequently inundated, making it susceptible to heavy metal contamination from past mining activities, industrial use, and agricultural runoff. The soil has a slightly alkaline pH of 7.2 (measured in $CaCl_2$) and a total organic carbon (TOC) content of 4.4%. Additionally, samples were taken from Neckarwestheim, situated directly on the eastern bank of the Neckar River. This area, formed by artificial embankments using heavy metal contaminated dredged material. The calcareous soil contains significant anthropogenic material and exhibits a slightly alkaline to neutral pH, with moderate organic content.

Finally, Field 26 of the Heidfeldhof (Experimental field station of the University of Hohenheim), has a notable history of heavy metal contamination due to the application of sewage sludge from 1972 to 1989, with an annual rate of 30 tons of dry matter per hectare. This long-term fertilization has resulted in significant heavy metal accumulation.

Soil properties, origin of the heavy metal contamination and Cd contents of the five soils are provided in Table 3.

Table 3. Soil properties and contamination history of experimental sites

Location	Soil texture	pH	Organic carbon content (g kg^{-1})	History of heavy metal contamination	Cd content (mg kg^{-1})
Braunschweig 1*	Silty sandy	5.8	10.6	Longterm wastewater irrigation	1.49
Braunschweig 2*	Silty sand	5.2	9.3	Longterm wastewater irrigation	0.49
Gundelsheim	Silty clay loam	7.2	50	Mining, industrial activities, agricultural runoff	12
Neckarwestheim	Silty clay loam	7.0	50.5	Dredged material, significant contaminated floodplain soil	47
Heidfeldhof	Silty loam	6.7	12.1	Historical application of sewage sludge	1.4

* Braunschweig 1 and Braunschweig 2 are topsoil samples from the raster cells I18 and N5, respectively, in (Ingwersen, 2001)

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To assess the mobility and bioavailability of heavy metals the soils were equilibrated with a 0.0025 M Calcium chloride ($CaCl_2$) background electrolyte and extracted with $CaCl_2$, EDTA and ammonium-nitrate. Each method targets different fractions of heavy metals in the soil, reflecting their environmental behavior and plant availability. $CaCl_2$ extraction gives a proxy of the heavy metal concentration in soil solution (mg L^{-1}) (McLaughlin et al., 2000). EDTA extraction gives an estimate of the heavy metals (mg kg^{-1}) participating in sorption-desorption processes (Meers et al., 2007). Ammonium-nitrate extraction is assumed to yield the bioavailable, i.e. plant-available fraction of heavy metals (mg kg^{-1}) (Cao et al., 2008).

Calcium chloride ($CaCl_2$) extraction was conducted to assess the concentration of heavy metal in the solution phase of soil. A triplicate of 10 grams of soil or soil-amendment mixtures was weighed into acid-rinsed (1 M HCl and 1 M HNO_3) 50 ml polypropylene centrifuge tubes containing 10 ml of 0.0025 M $CaCl_2$. The tubes were shaken on a vertically rotating shaker in an air-conditioned chamber at 22 ± 2 °C and 15 rpm (GLF overhead shaker 3040, LAUDA, Germany). After 24 hours of shaking, the soil suspension was centrifuged for 10 minutes at 4200 g (Thermo Scientific Sorvall RC-4, Langenselbold, Germany). The supernatant solution was filtered through a 0.45 µm membrane filter and stored in acid-rinsed polypropylene containers. To inhibit the sorption of dissolved heavy metals to the centrifuge tube walls, 500 µL of $(NH_4)_2$-EDTA was added to the solution. A 24-hour extraction with 0.0025 M $CaCl_2$ was found to be appropriate for approximating the concentration in the solution phase of their sandy soils (Streck and Richter, 1997).

EDTA (Ethylenediaminetetraacetic acid) was used to extract the total concentration of heavy metals that take part in sorption-desorption reactions (Filius et al., 1998; Gao et al., 2003). Triplicates of 2 grams of soil (sampled to a depth of 30 cm) were placed in acid-rinsed 50 ml polypropylene centrifuge tubes and mixed with 40 ml of 0.025 M $(NH_4)_2$-EDTA. The samples were shaken horizontally for 90 minutes at 140 rpm (horizontal shaker, KS-15, Edmund Bühler GmbH, Germany). Following the shaking, the mixture was centrifuged for 5 minutes at 1900 g (Thermo Scientific Sorvall RC-4, Langenselbold, Germany). The resulting suspension was then passed through a 0.45 µm membrane filter using a vacuum pump into acid-rinsed polypropylene tubes.

Ammonium-nitrate (AN) extraction was used to determine the plant available fraction of heavy metals in the soil samples. For this purpose, 2 g of soil were mixed with 50 ml of 1 M ammonium nitrate (NH4NO3) solution in acid-washed polypropylene centrifuge tubes and shaken for 24 hours on a vertical shaker at 15 rpm (GLF overhead shaker 3040, LAUDA, Germany) at room temperature (22 ± 2 °C). The mixture was then centrifuged at 1272 g for 15 minutes (Thermo Scientific Sorvall RC-4, Langenselbold, Germany), and the supernatant was filtered through a 0.45 µm membrane filter. The filtered samples were stabilized by adding 0.5 ml of concentrated HNO3 (65% p.a., Merck, No. 452) (Zeien and Brümmer, 1989).

After completing these three extractions, the filtered solutions were analyzed for metal concentrations (Cd, Cu, Zn, Ni, and Pb) using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (ICP-OES 5110, Agilent, Santa Clara, California, USA).

2.3 Statistical analysis

All statistical analyses were performed using a One-Way Analysis of Variance (ANOVA) at a significance level of 5% in OriginPro 24 (OriginLab Corporation). Following the ANOVA, Tukey's post-hoc test was applied to compare treatment means. The effects of soil amendments on plant-available water were evaluated separately for sandy and silty

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loam soils to account for texture-specific responses. To evaluate the potential of the amendments to reduce heavy metal uptake by plants, their effects on heavy metal mobility and plant availability were assessed by ANOVA based on total concentrations and extractable fractions. All ecotoxicological data were analysed separately for the two soils. The influence of soil amendments on cumulative CO_2 emissions was analysed at day 56 using one-way ANOVA. Similarly, microbial biomass and nitrogen mineralisation were assessed separately for the four time points (after 7, 14, 35 and 56 days), but time was not included as a factor in the ANOVA analysis. The behavioral responses of earthworms (after 28 days) and springtails (after 48 hours) were analyzed and compared to the control treatment using one-way ANOVA analysis to assess any ecological risks or benefits associated with the amendments.

3 Results

3.1 Experiment 1

3.1.1 Soil water retention and plant available water

The addition of SC_{plas} altered the shape of the water retention curves in both the sandy (Fig. 2A) and silty loam soil (Fig. 2B), while the other amendments showed no pronounced deviations from the control curve. The effect of SC_{plas} was soil-specific. In the sandy soil, SC_{plas} reduced the volumetric water content between pF 0 and pF 3 and the plant available water (PAW), whereas in the silty loam soil, SC_{plas} increased both quantities (Table 4). Similar to SC_{plas}, graphite increased plant available water in the silty loam soil. Solid carbon from catalytic pyrolysis SC_{cat}, and the biochar did not change the amount of plant available water compared to the control s

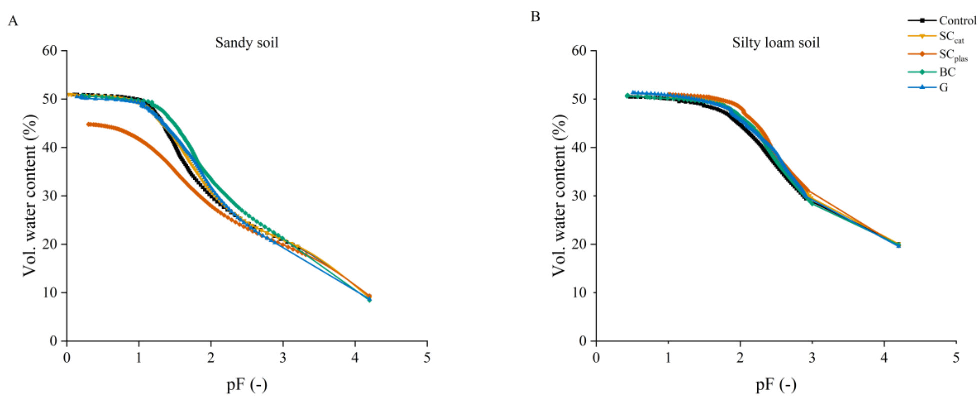

Figure 2. Effect of soil amendments on water retention curves in (A) sandy and (B) silty loam soil. Treatments were: C: control, SC_{cat}: solid carbon from catalytic pyrolysis, SC_{plas}: solid carbon plasma pyrolysis, BC: Biochar, G: Graphite

Table 4. Effect of the carbon amendments on physical soil characteristics. Values represent the mean ± standard error, where n=4 for plant available water and n=3 for air capacity, volumetric water content at field capacity, and volumetric water content at permanent wilting point. Statistical differences between treatments within each soil type are indicated by different letters (a, b, c), with values sharing the same letter not significantly different from each other ($P < 0.05$,

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ANOVA analysis followed by a post-hoc test). Plant available water calculations assume a plowing horizon thickness
295 of 0.3 m.

	Treatments	Porosity (%)	Air capacity (vol %) at pF 1.8	Volumetric water content at field capacity (vol %) at pF 1.8	Volumetric water content at permanent wilting point (vol %) at pF 4.2	Plant available water (mm, L m^{-2})
Sandy soil	Control	50.9	17.4 ± 0.1^{b}	33.5 ± 0.1^{b}	9.2 ± 0.05^{a}	71.1 ± 0.7^{b}
	SC_{cat}	50.9	15.7 ± 0.3^{b}	35.2 ± 0.3^{b}	8.9 ± 0.2^{a}	75.6 ± 3.3^{b}
	SC_{plas}	50.9	20.5 ± 1.1^{a}	30.5 ± 1.1^{c}	9.4 ± 0.02^{a}	63.0 ± 1.2^{c}
	Biochar	50.9	12.7 ± 0.1^{c}	38.2 ± 0.1^{a}	8.4 ± 0.4^{a}	88.8 ± 0.3^{a}
	Graphite	50.9	15.6 ± 0.7^{b}	35.3 ± 0.7^{b}	8.7 ± 0.1^{a}	78.3 ± 1.6^{b}
Silty loam soil	Control	50.9	3.3 ± 0.4^{a}	47.5 ± 0.4^{b}	20.1 ± 0.1^{a}	83.1 ± 1.6^{b}
	SC_{cat}	50.9	2.3 ± 0.1^{ab}	48.6 ± 0.1^{ab}	20.1 ± 0.03^{a}	85.5 ± 0.2^{ab}
	SC_{plas}	50.9	1.8 ± 0.3^{b}	49.2 ± 0.3^{a}	19.7 ± 0.2^{a}	88.5 ± 0.9^{a}
	Biochar	50.9	2.5 ± 0.03^{ab}	48.4 ± 0.03^{ab}	19.9 ± 0.01^{a}	85.5 ± 0.2^{ab}
	Graphite	50.9	2.4 ± 0.3^{ab}	48.6 ± 0.2^{ab}	19.6 ± 0.1^{a}	87 ± 0.9^{a}

SCcat: solid carbon from catalytic pyrolysis, SCplas: solid carbon from plasma pyrolysis

3.1.2 Hydraulic conductivity

The addition of SC_{plas} altered the shape of the hydraulic conductivity curves in both the sandy (Fig. 3A) and the silty loam soil (Fig. 3B), while the other amendments led to less pronounced deviations from the control. The effect of SC_{plas}

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differed between the two soils. In the sandy soil, hydraulic conductivity decreased across most of the pF range. In contrast, in the silty loam soil, SC_{plas} showed a marginal reduction in hydraulic conductivity, particularly at lower pF. SC_{cat} showed a slight increase in hydraulic conductivity in both soils compared to the control, particularly at lower pF in the sandy soil. Biochar consistently increased hydraulic conductivity in both the sandy and the silty loam soil, with more pronounced effects at lower pF. Graphite similarly enhanced hydraulic conductivity, albeit to a lesser extent than biochar, in both soils, indicating moderate increase in water flow at given hydraulic gradient.

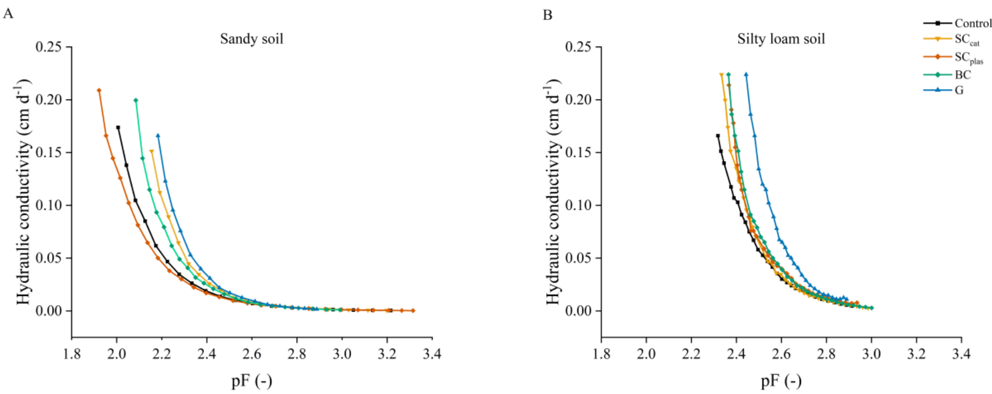

Figure 3. Hydraulic conductivity functions in (A) sandy and (B) silty loam soil as influenced by different soil amendments. Treatments were: C: control, SC_{cat}: solid carbon from catalytic pyrolysis, SC_{plas}: solid carbon from plasma pyrolysis, BC: Biochar, G: Graphite

3.1.3 Ecotoxicological tests

Compared to the control, cumulative CO_2 emissions were more pronounced for soil treatments with reference materials than with solid carbons derived from catalytic pyrolysis and plasmalysis (except for solid carbons from plasmolysis in silty loam soil) (Fig. 4). The solid carbon materials produced by catalytic and plasma pyrolysis did not significantly affect the cumulative CO_2 emissions in the sandy soil after 56 days of incubation in comparison to the control, while biochar and graphite increased CO_2 production (Fig. 4A). In the silty loam soil, none of the amendments increased CO_2 production, but SC_{cat} and SC_{plas} slightly reduced it (Fig. 4B). As expected, CO_2 production was highest during the first few days of incubation, after which it declined. (Fig. S1A and B).

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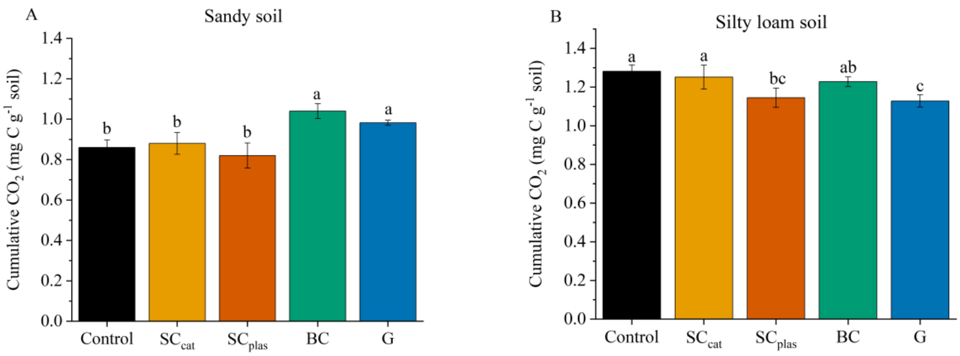

Figure 4. Cumulative CO_2 evolved during 56 days of incubation after addition of 40 t ha^{-1} test material (mean and standard error, n = 4). Treatments were C: control, SC_{cat}: solid carbon from catalytic pyrolysis, SC_{plas}: solid carbon plasma pyrolysis, BC: Biochar, and G: Graphite. Different lowercase letters represent significant differences between treatments at $p < 0.05$.

Microbial biomass (C_{mic}) was generally higher in the silty loam than in the sandy soil and rather stable over time (Fig. 5A and B). None of the added material induced a significant effect on C_{mic} during the 56 days of incubation.

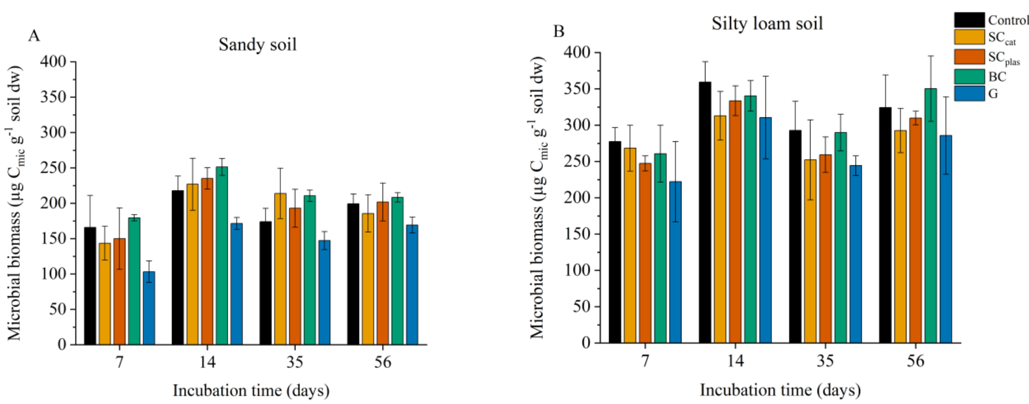

Figure 5. Microbial biomass during 56 days of incubation after addition of 40 t ha^{-1} test material (mean and standard error, n = 4). Treatments were: C: control, SC_{cat}: solid carbon from catalytic pyrolysis, SC_{plas}: solid carbon plasma pyrolysis, BC: Biochar, and G: Graphite. No statistically significant difference between treatments and incubation times was detected at $p < 0.05$.

Regarding extractable organic C (EOC), SC_{plas} significantly reduced EOC in both soils, whereas SC_{cat} reduced EOC in sandy soil only on day 14, and in silty loam soil on days 7 and 56 (Fig. 6A and B). Biochar reduced EOC on days 14

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and 35 in sandy soil, and did not affect EOC in silty loam soil, while graphite, on the contrary, did not affect EOC in sandy soil, and in silty loam soil at the end of the experiment (day 56) reduced EOC.

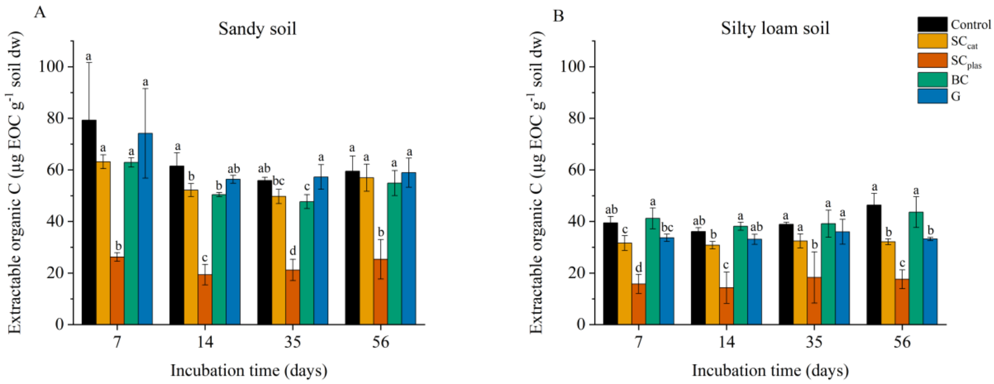
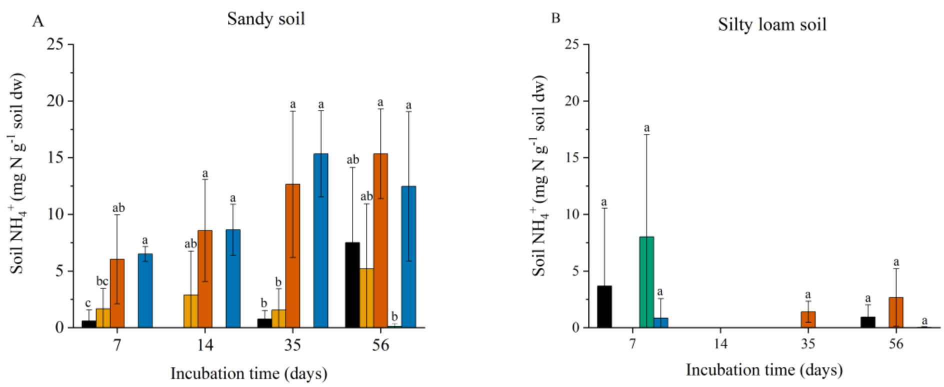


Figure 6. Extractable organic C (EOC) during 56 days of incubation after addition of 40 t ha^{-1} test material (mean and standard error, n = 4). Treatments were: C: control, SC_{cat}: solid carbon from catalytic pyrolysis, SC_{plas}: solid carbon plasma pyrolysis, BC: Biochar, and G: Graphite. Different lowercase letters represent a significant difference at p < 0.05 between treatments at a given sampling day (7, 14, 35, or 56).

For N mineralization in the sandy soil, SC_{plas} and graphite increased NH4+-N content up to day 35 significantly and tended to increase NH4+-N at 56 days of incubation in comparison to the control. (Fig. 7A). In the silty loam NH4+-N content was generally lower than in the sandy soil and there were no statistically significant differences between the materials (Fig. 7B).

The addition of SC_{cat} to the sandy soil did not have a significant effect on the nitrate content, while SC_{plas} led to a decrease of the nitrate nitrogen content during the entire incubation period (Fig. 7C). Soils with reference materials showed an initial (up to 35 days) decrease of nitrate content, which leveled out over time, reaching the control level at day 56 (Fig. 7C). In silty loam soil, only the addition of graphite increased the content of nitrate significantly in comparison to the control, while the other materials (SC_{cat}, SC_{cat}, biochar) decreased nitrate contents starting from day 14 on (Fig. 7D).



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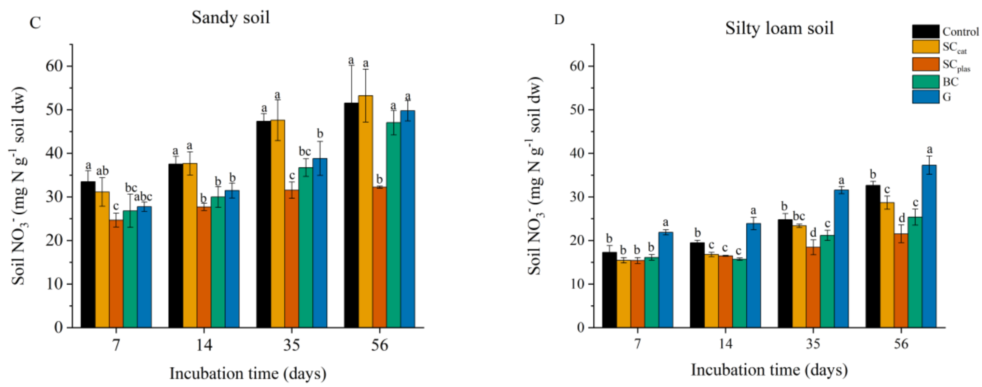

Figure 7. Concentrations of ammonium and nitrate ions during 56 days of incubation after addition of 40 t ha^{-1} test material (mean and standard error, n = 4). Treatments were: C: control, SC_{cat}: solid carbon from catalytic pyrolysis, SC_{plas}: solid carbon plasma pyrolysis, BC: Biochar, and G: Graphite. Different lowercase letters represent a significant difference at $p < 0.05$ between treatments at the four sampling days (7, 14, 35, 56).

In terms of avoidance test with earthworms, all specimens survived the 28 days of incubation in control and amended soils. In the sandy soil, the avoidance test showed a significant avoidance of endogenous earthworms against soils amended with SC_{plas} and graphite, but not against soils amended with SC_{cat} or biochar (Fig. 8A).
In the silty loam soil, earthworm behavior was different. Here the earthworms significantly avoided burrowing when biochar or graphite were present but showed no avoidance against SC_{cat} and SC_{plas} (Fig. 8B).

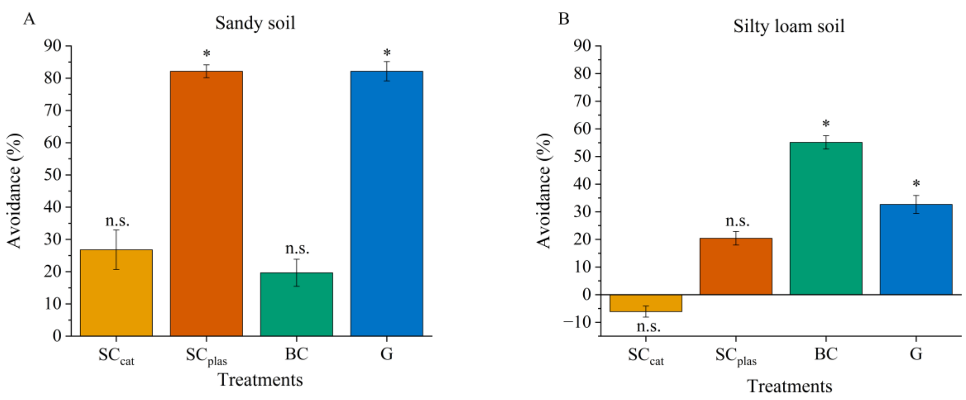

Figure 8. Ecotoxicological avoidance test with endogenic earthworms in soils amended with 40 t ha^{-1} solid carbon from catalytic pyrolysis (SC_{cat}) and solid carbon from plasma pyrolysis (SC_{plas}), biochar (BC), graphite (G) in comparison to the control soils without amendments n = 7. The symbol * represents a significant difference compared to the control at $p < 0.05$, n.s. = not significant.

Regarding avoidance test with springtails, all specimens survived the 2 days of incubation in the control and amended soils. The avoidance test in the sandy soil showed significant avoidance of *F. candida* against soils amended with

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reference materials (biochar and graphite), but there was no avoidance against SC_{cat} and SC_{plas} (Fig. 9A). In the silty loam soil, the behavior of *F. candida* was different only for SC_{plas}. With $SC_{plas,}$ springtails largely avoided soils, as well as with biochar or graphite, but they did not show avoidance against SC_{cat} (Fig. 9B).

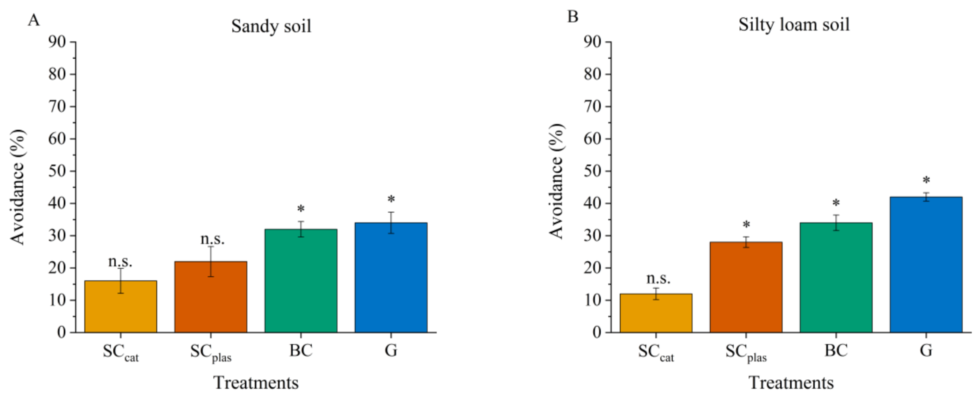

Figure 9. Ecotoxicological avoidance test with springtails in soils amended with 40 t ha^{-1} solid carbon from catalytic pyrolysis (SC_{cat}) and solid carbon from plasma pyrolysis (SC_{plas}), biochar (BC), graphite (G) in comparison to the control soils without amendments (n = 5). The symbol * represents a significant difference compared to the control at $p < 0.05$, n.s. = not significant.

3.2 Experiment 2

3.2.1 Heavy metal fraction in soil solution

The effects of soil amendments on heavy metal concentrations in 0.0025 M $CaCl_2$ solution varied by metal and site, with SC_{plas} consistently demonstrating a strong immobilizing effect. SC_{plas} significantly reduced Cd concentrations in Braunschweig 1 and Braunschweig 2 soils, whereas SC_{cat} increased Cd availability at these sites. In Gundelsheim, both SC_{plas} and SC_{cat} reduced Cd levels, while no significant differences between treatments were observed at Neckarwestheim (Fig. 10A). For Cu, SC_{plas} consistently decreased concentrations at Braunschweig 1, Braunschweig 2, and Neckarwestheim, outperforming SC_{cat} and the other amendments, which showed no significant deviations from the control (Fig. 10B). SC_{plas} also reduced Ni concentrations most effectively at Braunschweig 1 and Braunschweig 2, while SC_{cat} and the other amendments had negligible effects (Fig. 10C). For Zn, biochar was the most effective amendment, significantly lowering concentrations at Braunschweig 1 and Braunschweig 2, while SC_{plas}, SC_{cat}, and graphite had minimal influence. At Neckarwestheim, Zn concentrations were consistently low across all treatments, suggesting limited amendment effects at this site (Fig. 10D).

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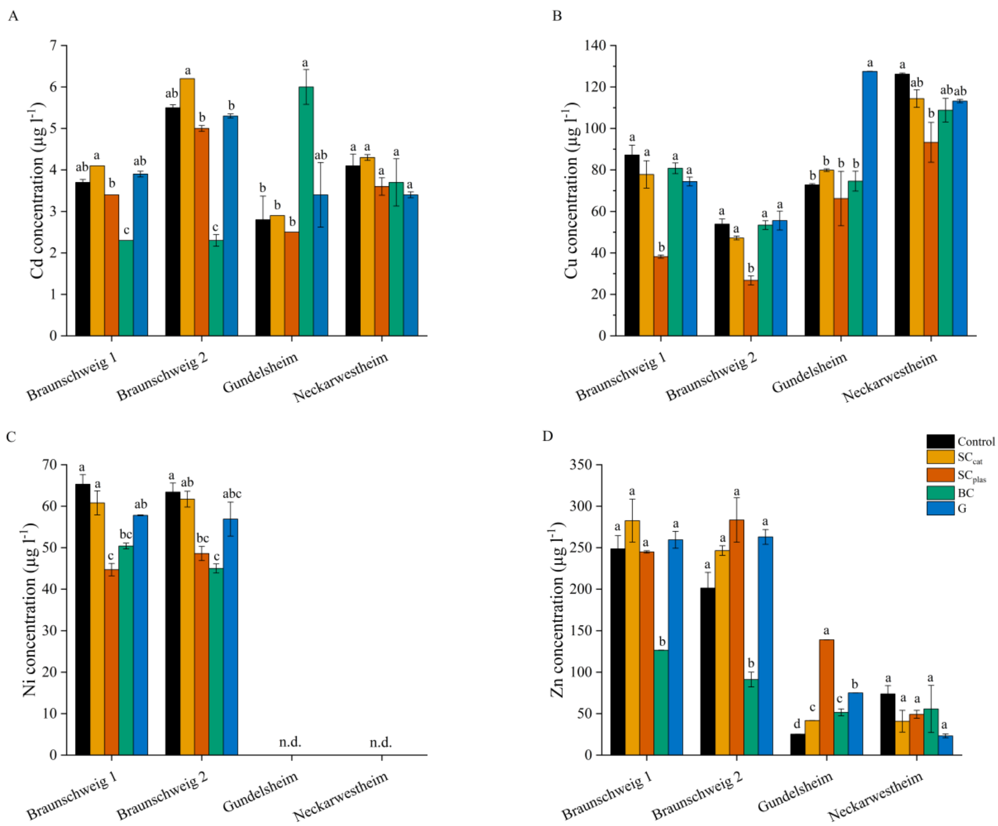

Figure 10. Effect of different soil amendments on heavy metal concentration (Cd, Cu, Ni, Zn) in 0.0025 M $CaCl_2$ solution across various sites (mean and standard error, n = 2). Treatments were: C: control, SC_{cat}: solid carbon from catalytic pyrolysis, SC_{plas}: solid carbon from plasma pyrolysis, BC: Biochar, G: Graphite. Results below the detection limit are indicated by "n.d.". Note: The data for Heidfeldhof are not shown because all measured concentrations were below the detection limit.

3.2.2 Plant available heavy metal fraction

The effects of soil amendments on plant available heavy metal concentrations, as determined by ammonium nitrate extraction, varied by metal and site. SC_{plas} consistently demonstrated a strong immobilizing effect. For Cd, biochar significantly reduced concentrations at Braunschweig 1 and Braunschweig 2, while SC_{plas}, SC_{cat}, and graphite showed no significant deviations from the control at these sites. In contrast, no measurable treatment effects were observed at Gundelsheim and Neckarwestheim, where Cd levels remained consistent across all amendments (Fig. 11A). For Cu, SC_{plas} achieved the most pronounced reductions at Gundelsheim and Neckarwestheim, while SC_{cat}, biochar, and graphite exhibited slightly lower concentrations than the control but were not statistically significant (Fig. 11B). For Ni, SC_{plas}, biochar, and graphite reduced concentrations below detection limits at Neckarwestheim, while detectable levels were observed only in the control and SC_{cat}. At Braunschweig 1 and Braunschweig 2, Ni concentrations were

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stable across all treatments, with no significant differences (Fig. 11C). For Zn, SC_{plas} exhibited the highest concentrations at Heidfeldhof, though differences from the control and SC_{cat} were not significant. Biochar significantly reduced Zn concentrations compared to SC_{plas} at Heidfeldhof, while no significant effects of amendments were observed at Braunschweig 1, Braunschweig 2, Gundelsheim, or Neckarwestheim, where concentrations remained consistent across treatments (Fig. 11D).

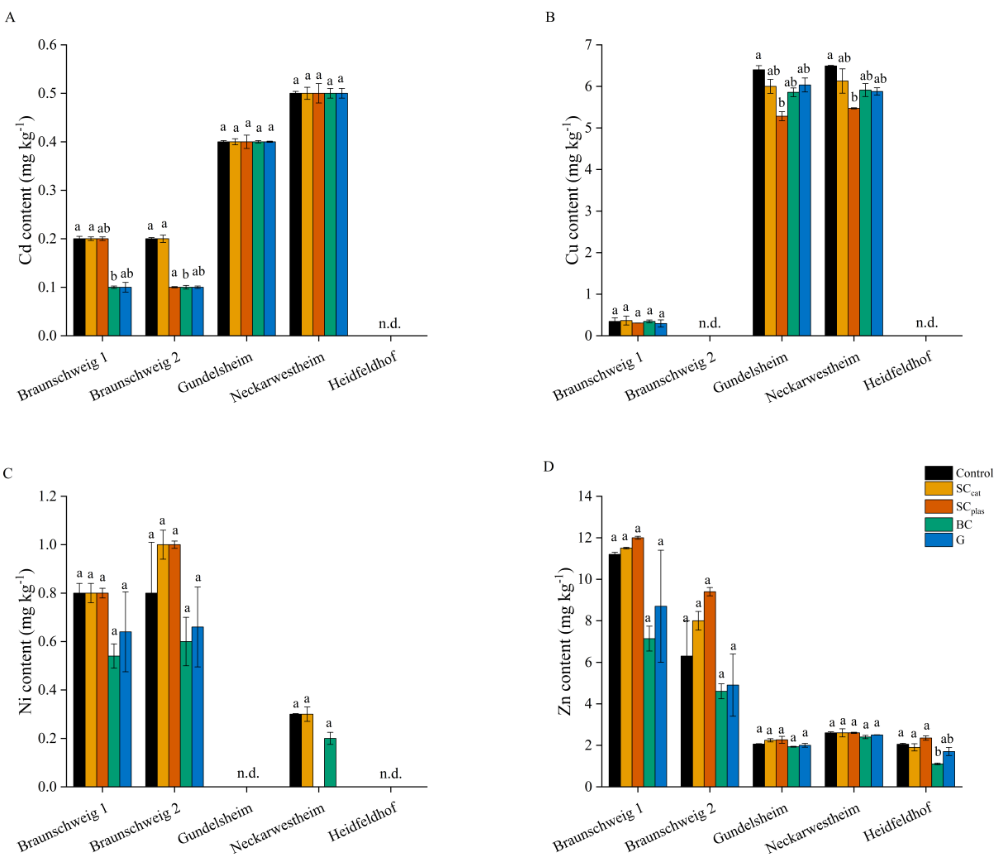

Figure 11. Effect of soil amendments on plant-available Cadmium (Cd), Copper (Cu), Nickel (Ni), and Zinc (Zn) concentrations across various sites as determined by ammonium nitrate extraction. Treatments were: C: control, SC_{cat}: solid carbon from catalytic pyrolysis, SC_{plas}: solid carbon from plasma pyrolysis, BC: Biochar, G: Graphite. Bars represent mean values ± standard error, n=2. Statistical differences are indicated by letters above the bars ($P < 0.05$, based on ANOVA analysis). Sites with concentrations below the detection limit are marked as n.d. (not detected).

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4 Discussion

4.1 Influence of different solid carbon materials on soil water retention and hydraulic conductivity

With $SC_{plas,}$ the water retention curve (Fig. 2A) showed a decrease in volumetric water content across different matric potentials. The reduction cannot be explained by a change in porosity, as the total porosity remained constant among all treatments (50.9%). Instead, the observed differences are likely due to a decrease in air capacity (Table 4). A plausible explanation for this pattern is that SC_{plas} aggregates within the soil matrix, creating stone-like clusters that block pore connectivity and hinder water retention (Ajayi and Horn, 2016; Hardie et al., 2014). Consequently, this would result in a faster drainage of water, making less water available for plant uptake.

The reduction in plant available water by about 5 mm would shorten the period of water availability for plants by 1–2 days, assuming typical evapotranspiration rates of 3–5 (mm day^{-1}) for actively growing crops under moderate climatic conditions (Ritchie, 1981). Although this effect is small, it highlights the importance of evaluating long-term implications, particularly in drought-prone environments where even minor changes in soil moisture retention can impact crop productivity. Despite these changes, the medium pores, which control plant available water, did not undergo major modifications. This suggests that the overall soil structure was largely preserved, with the observed differences primarily attributed to localized aggregate formation rather than a fundamental shift in pore size distribution.

SC_{plas} also altered hydraulic conductivity, particularly in the sandy soil, where conductivity decreased across most matric potentials (Fig. 3A). This reduction was most notable at the pF< 1.8, corresponding to large pores, which hold water under near saturated conditions. The increase in air capacity (Table 4) supports these results, indicating that air-filling of large pores limit water flow. These findings align with (Bordoloi et al., 2021), who observed similar reductions in hydraulic conductivity when hydrophobic amendments altered soil pore structure. (Bordoloi et al., 2021) investigated how structural changes in porous media influence fluid transport and dispersion, particularly in relation to anomalous flow behavior caused by vortices and pore-scale structures. Their study emphasized that disruptions in pore connectivity could lead to localized flow restrictions, creating regions of stagnation or preferential flow paths.

Other than in the sandy soil, SC_{plas} significantly increased plant available water in the silty loam soil. The higher organic matter content and finer texture of the silty loam soil likely mitigated the pore blocking effects observed in the sandy soil. Instead of disrupting pore connectivity, SC_{plas} may have enhanced water retention by interacting with finer soil particles and colloids, which stabilized water films and improved capillary water storage (Chen et al., 2012; Eibisch et al., 2015). Hydraulic conductivity in the silty loam soil exhibited only a marginal reduction, primarily at low pF (Fig. 3B). We assume that the greater field capacity of the silty loam soil makes it less affected by hydrophobicity induced pore disruption.

SC_{cat} had no significant influence on plant available water in either soil texture. This is likely due its low porosity and high crystallinity, characteristics of carbon produced at high pyrolysis temperatures (~950°C) from biogas or methane (Brewer et al., 2014). Unlike biochar, which has a highly porous structure (Yu et al., 2013), SC_{cat} lacks the fine pores necessary for improving soil water retention.

However, SC_{cat} moderately increased hydraulic conductivity in the sandy soil, particularly in the range of pF 1.8 - 2.5, where narrower pores dominate water flow. This indicates that SC_{cat} increased pore connectivity, facilitating water movement at moderate matric potentials without significantly altering the retention capacity of the soil. This suggests that SC_{cat} may be useful for improving infiltration in sandy soils, particularly in scenarios where rapid water drainage is desired. In the silty loam soil, SC_{cat} had an even smaller effect on conductivity, probably due to the already well-connected pore system of the soil.

These results are consistent with those of (Blanco-Canqui, 2017), who reported that carbon-based soil amendments have varying effects on water retention and hydraulic conductivity depending on their structure, porosity, and interaction with soil texture. The moderate increase in conductivity observed with SC_{cat} makes it useful as an amendment when small improvements in infiltration are desired, but less suitable for drought-prone conditions.

4.2 Effects of solid carbon materials on soil properties and soil organisms

Incorporation of SC_{cat} did not affect soil respiration, regardless of soil texture. This indicates that the carbon from catalytic pyrolysis is not available to microorganisms, probably due to the high crystallinity of the material. In silty loam soil, a similar effect was observed when biochar was applied, which was used as a reference material in our study. However, in the sandy soil, biochar led to an increase in soil respiration, which is consistent with other studies (Gao et al., 2020).

The effect of SC_{cat} on extractable organic carbon (EOC) and mineral nitrogen depends on soil texture. In the sandy soil, SC_{cat} had no significant effect on the level of EOC and nitrate, which may indicate its weak interaction with organic and inorganic soil components due to its low porosity and small surface area. Biochar, unlike SC_{cat}, showed significantly higher sorption in sandy soil, which is due to its amorphous structure, high porosity and much higher specific surface area (Beesley et al., 2010; Pietikäinen et al., 2000; Yang et al., 2016). According to (Jing et al., 2022; Yao et al., 2014), the presence of clay particles on the surfaces of pyrogenic carbon can dramatically increase (by about 5 times) the adsorption capacity, which is mainly controlled by ion exchange (with clay) and electrostatic attraction (with biochar) (Jing et al., 2022; Yao et al., 2014). A decrease in the concentration of nitrate ions in the silty loam was observed from 14 days on. Although the temporal pattern of the effect of biochar on nitrate depended on soil texture, biochar generally decreased nitrate concentrations. This is in line with the results of other studies that indicate that biochar can reduce the leaching of inorganic nitrogen through adsorption (Liu et al., 2018; Major et al., 2012; Sun et al., 2017; Yao et al., 2012).

Earthworms and springtails showed no avoidance or sign of toxicity in SC_{cat}-treated soil. This indicated that PAHs, which have been shown to negatively affect the quality of earthworm habitat in soils (Jonker et al., 2004) are not relevant here. Indeed, the analysis of PAHs in SC_{cat} showed low concentrations of phenanthrene (0.097 mg kg^{-1}) and pyrene (0.01 mg kg^{-1}).

The effects of biochar contrasted with those of SC_{cat}. This may depend on differential effects of biochar in soils with different pH. In the experiment of (Van Zwieten et al., 2010), earthworms preferred sandy soil with a pH of 5.1 supplemented with biochar, but avoided it in silty loam soil with a pH of 6.9. This is in line with other authors who indicate that biochar can cause a sharp increase in pH, making it less suitable for certain soil fauna (Liesch et al., 2010). This is especially critical for *F. candida*, as the increased pH can affect the microbiota composition, reducing the number of fungi that are the main food source for springtails (Jänsch et al., 2005; Rousk et al., 2009).

Thus, the main advantage of SC_{cat} as soil amendment is its neutral effect on the acid-base balance of the soil, which makes it a more environmentally inert material compared to biochar. Its high crystallinity and low reaction surface

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likely ensure long-term stability in the soil (Table 1. Characteristics of the studied solid carbon materials), as a poor biodegradability is indicated by the non-enhanced CO_2 production within the first 56 days after addition to soils. However, its low porosity and significantly lower specific surface area (Table 1. Characteristics of the studied solid carbon materials) can limit the ability for microbial colonization and adsorbance of nutrients.

In the sandy soil, SC_{plas} had no effect on soil respiration or microbial biomass, while graphite stimulated soil respiration. In case of graphite, this could be due to an increase of field capacity of the soil as a result of the formation of additional mesopores in the sandy soil (Du et al., 2024), while SC_{plas} did not lead to additional mesopores (Table 1). In silty loam soil, SC_{plas} reduced soil respiration. This was probably due to decreased oxygen supply, which limited the access of oxygen to microorganisms and, accordingly, slowed down the aerobic decomposition of soil organic matter. A similar effect was observed with graphite, indicating possible common mechanisms for this effect.

The inhibition of microbial respiration may be partly due to toxic effects of residual PAHs in SC_{plas} (phenanthrene 2.55 mg kg^{-1}, pyrene 1.72 mg kg^{-1}). These can act as antimicrobial agents, as PAHs can negatively affect the structure of the bacterial cell membrane and bacterial metabolism (Bramwell and Laha, 2000). The fact that this effect did not occur in the sandy soil indicates that the main factor was limited gas exchange and less access of microorganisms to the organic substrate. The latter is supported by a significant decrease in the concentration of extractable organic carbon (EOC), as easily accessible source of carbon for microbial mineralization. On the other hand, SC_{plas} in sandy soil also resulted in a decrease in the content of EOC, but this did not decrease microbial activity and soil respiration. This finding may be explained by the lower abundance of microorganisms in sandy soil. The data also indicate that SC_{plas} had a higher adsorption capacity than graphite, as it reduced the content of EOC in both soils, while graphite reduced it only in silty loam soil.

At the same time, the presence of residual PAHs in SC_{plas}, which could act as nitrification inhibitors (Zhou et al., 2018), probably caused disruption of nitrification processes and led to the accumulation of ammonium ions up to 35 days in sandy soil and on day 35 in silty loam soil. This resulted in a decreased nitrate concentration in sandy soil throughout the experiment, and in silty loam soil at day 14.

The response of earthworms to SC_{plas} varied depending on the soil. In sandy soil, they showed avoidance, which may be related to the presence of PAHs. A study by (Wu et al., 2012) found that high doses of phenanthrene and pyrene in soil resulted in growth inhibition and decrease in earthworm biomass (Wu et al., 2012). In addition, the disruption of nitrification in sandy soil and the accumulation of ammonium ions may also have induced an avoidance reaction by the earthworms. Earthworms are known to be sensitive to toxic compounds, as they are constantly in contact with large volumes of soil during digging and ingest soil particles, and they breathe through their skin, which is permeable for many chemical compounds (Esmaeili et al., 2022). In the silty loam soil, the toxic effect of SC_{plas} was likely to be neutralized by the high adsorption capacity of clay particles, which could bind PAHs and reduce their bioavailability (Yu et al., 2014). In addition, earthworms in SC_{plas}-supplemented soil lost biomass, which may correlate with the natural survival strategy of earthworms, in which food consumption is reduced to avoid toxins. Differences in the ecotoxicological responses of *F. candida* compared to earthworms may be related to differences in their ecological niche and physiology. Springtails live mainly in the upper layers of soil or on its surface, so their contact with contaminated environments is less intense compared to earthworms. In addition, their chitinous exoskeleton provides a certain level of protection against toxic compounds (Nickerl et al., 2014). Accordingly, these organisms are less

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sensitive to pollution and did not avoid the sandy soil supplemented with SC_{plas}. Our results indicate that the springtails avoidance strategy depended more on microbial activity than on the presence of toxic substances. Since SC_{plas} did reduce microbial activity in the sandy soil, it did not cause springtails to avoid this environment. However, in the silty loamy soil, where microbial activity was reduced, springtails showed avoidance, which may be due to changes in resource availability (Domene et al., 2007).

Regardless of the soil texture, graphite has a negative impact on soil fauna, possibly through nutrient adsorption, mechanical impact, changes in water balance and alteration of the microbial environment (Ahmed and Rodrigues, 2013; Chen et al., 2014; Hammerschmiedt et al., 2023; Liu et al., 2011). This makes it an unfavorable substance for soil organisms such as earthworms and springtails, which are sensitive to changes in the physical, chemical and biological properties of the soil (Didden and Römbke, 2001; Greenslade and Vaughan, 2003).

4.3 Influence of solid carbon materials on heavy metal concentrations in soil solution

Heavy metal concentration in 0.0025 M $CaCl_2$ showed significant variations among the tested materials. Notably, SC_{plas} consistently demonstrated a strong immobilizing effect across sites, particularly for cadmium (Cd). This aligns with findings by other studies (Hussain et al., 2020) that link the effectiveness of carbon-based amendments to their specific physicochemical properties, such as surface functional groups and porosity, which can facilitate heavy metal adsorption and complexation.

For Cd, SC_{plas} significantly reduced soil solution concentrations in Braunschweig 1 and Braunschweig 2 soils, whereas SC_{cat} increased its mobility. The enhanced immobilization by SC_{plas} may be attributed to its enhanced cation exchange capacity (CEC) and affinity for Cd ions. Conversely, SC_{cat} may have introduced responsible organic components and has a lower surface area anyway, thus resulting in increased Cd solubility (Blanco-Canqui, 2017). In Gundelsheim soil, both SC_{plas} and SC_{cat} reduced Cd levels, indicating a site-specific interaction between amendment properties and soil characteristics. This variability underscores the importance of considering soil texture and pH in amendment selection, as highlighted by (Wei et al., 2023). In contrast, in Neckarwestheim soil, where Cd concentrations were inherently low, no significant differences were observed between treatments, suggesting limited amendment effects in uncontaminated soils.

For copper (Cu), SC_{plas} consistently outperformed other amendments by significantly reducing soil solution concentrations in most soils. This can be attributed to its high surface reactivity and functional group diversity, which enhance its Cu-binding capacity. Similar findings for carbon amendments with high reactivity have been reported by (Faloye et al., 2024). SC_{cat} and the other amendments showed negligible effects on Cu, pointing at their limited availability of reactive binding sites.

Nickel (Ni) concentrations were most effectively reduced by SC_{plas}, particularly in Braunschweig 1 and Braunschweig 2 soils, while SC_{cat} and other amendments had minimal effects. The Ni-binding efficiency of SC_{plas} could stem from its high cation exchange properties and the presence of functional groups conducive to strong Ni complexation. This finding is consistent with studies indicating the importance of amendment-specific functional chemistry in heavy metal stabilization (Hussain et al., 2020).

For zinc (Zn), biochar emerged as the most effective amendment in Braunschweig 1 and Braunschweig 2 soils, significantly lowering Zn concentrations. The porous structure and surface chemistry of biochar likely facilitated Zn

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adsorption. These findings align with previous research by (Edeh et al., 2020) and (Villagra-Mendoza and Horn, 2018), which emphasized biochar's ability to immobilize Zn in coarse-textured and degraded soils. However, SC_{plas}, SC_{cat}, and graphite exhibited minimal influence on Zn concentrations, implying their limited capacity for Zn immobilization under the tested conditions. In Neckarwestheim soil, Zn concentrations were inherently low, likely below the threshold where amendment effects become detectable, thereby resulting in negligible responses. Additionally, soil properties such as higher pH and organic matter content at this site may have naturally limited Zn mobility, further reducing the potential for amendments to exhibit noticeable effects.

4.4 Influence of solid carbon materials on plant availability of heavy metals

For Cd, biochar exhibited significant reductions in plant available concentrations in Braunschweig 1 and Braunschweig 2 soils, while SC_{plas}, SC_{cat}, and graphite showed no significant deviations from the control. These findings are consistent with (Edeh et al., 2020), who observed biochar's ability to immobilize heavy metals through its porous structure and high cation exchange capacity (CEC). The limited effect of SC_{plas} and SC_{cat} at these sites suggests that their physicochemical properties may not be as conducive to Cd immobilization under AN extraction condition. In Gundelsheim and Neckarwestheim soils, no measurable effects of amendments were observed, likely due to low baseline Cd concentrations at these locations. Such low initial concentrations of Cd can reduce the detectability of any amendment effects. Additionally, these two sites had a higher content of organic matter and a higher soil pH compared to the Braunschweig sites. These characteristics are known to naturally reduce the mobility of Cd, which further diminishes the observable influence of amendments (Hussain et al., 2020).

SC_{plas} achieved the most pronounced reductions of plant-available Cu concentrations in Gundelsheim and Neckarwestheim soils. The immobilizing effect may originate from its abundant reactive surface functional groups, which enhances Cu adsorption and complexation. Our findings are consistent with previous studies (Faloye et al., 2024), which highlight the effectiveness of reactive carbon-based amendments in immobilizing Cu. In contrast, SC_{cat}, biochar, and graphite reduced Cu concentrations only slightly and reductions were not statistically significant.

SC_{plas}, biochar, and graphite reduced Ni concentrations below detection limits in Neckarwestheim soil, demonstrating their potential for effective Ni immobilization in specific soils. (Wei et al., 2023) emphasized the importance of soil texture and amendment reactivity in determining heavy metal immobilization outcomes. The absence of detectable Ni in these treatments suggests a synergistic interaction between amendment properties and soil conditions, such as pH and organic matter. In Braunschweig 1 and Braunschweig 2 soils, amendment effects were minimal. It is not clear what reduced the effectiveness of amendments there.

The impact of amendments on Zn concentrations was highly site-dependent. In Heidfeldhof soil, SC_{plas} reduced Zn concentrations least, with no statistically significant difference from the control or SC_{cat} treatments. In contrast, biochar significantly reduced Zn concentrations, suggesting its superior capacity for Zn immobilization, probably because of its high porosity and surface reactivity. These findings are consistent with earlier studies highlighting biochar's efficacy in reducing Zn bioavailability in contaminated soils (Edeh et al., 2020; Villagra-Mendoza and Horn, 2018). In other soil (Braunschweig 1, Braunschweig 2, Gundelsheim, and Neckarwestheim), Zn concentrations remained consistent across treatments, reflecting limited amendment effects under these conditions. This outcome emphasizes the variability in amendment performance based on site-specific factors, which could be baseline Zn levels, soil mineralogy, texture and competing ions.

5 Conclusions

This study provides a comprehensive assessment of the effects of solid carbon materials derived from catalytic pyrolysis (SC_{cat}) and plasma pyrolysis (SC_{plas}) on soil water retention, hydraulic conductivity, soil respiration, C and N dynamics and soil organisms, and heavy metal immobilization.

SC_{cat} had no significant effect on water retention but moderately increased hydraulic conductivity in the sandy soil. SC_{cat} may improve water infiltration without improving moisture retention. It had virtually no significant effect on soil biological parameters, regardless of soil texture, which may indicate its minimal impact on soil ecosystems. In heavier soils, it can improve soil structure, reduce soil density and increase air and moisture availability. At the same time, compared to biochar, SC_{cat} is less active in its interaction with organic matter and mineral components of the soil, which may limit its functionality in certain ecosystems. However, in soils contaminated with heavy metals, SC_{cat} increased Cd mobility at some sites, indicating little or even adverse effects on heavy metal stabilization.

SC_{plas}, in contrast, had contrasting effects on plant available water depending on soil texture. It may not be suitable for sandy soils due to its effect on pore connectivity. SC_{plas} can have negative impacts on both soil organisms and soil carbon and nitrogen cycling. This is due to its high sorption capacity and the fact that it may contain residual PAHs. Nevertheless, in soils contaminated with heavy metals, SC_{plas} consistently strongly immobilised the heavy metals, particularly Cd, Cu and Ni.

Based on these findings, the use of solid carbon materials derived from methane pyrolysis as a soil amendment has mixed prospects. While SC_{cat} represents a safe soil amendment with minimal environmental risks, its limited benefits and potential adverse effects on heavy metal mobility restrict its general applicability. SC_{plas} shows promise specifically for heavy metal contaminated sites due to its superior immobilization capacity, but its negative impacts on soil biota raise concerns about a widespread application.

Overall, we conclude that SC_{cat} is a safe soil amendment, but with little or adverse effects on heavy metal mobility in contaminated soils. In contrast, SC_{plas} immobilises heavy metals, but its amendment must be carefully considered in light of possible negative effects.

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