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Electrical conductivity of biochar: method optimization and insights from an industrial data set

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ABSTRACT

Depending on its condensed aromatic structures, biochar varies in electrical conductivity. Measuring this conductivity allows to conclude about carbon speciation and, indirectly, about pyrolysis conditions. Recently, the electrical conductivity of dried and non-suspended biochar, termed as solid-state electrical conductivity (SEC), has been adopted as an analytical parameter in the European Biochar Certificate and is now proposed by several commercial and academic laboratories as routine analysis. Here, we present the corresponding measurement setup and test its limitations. Electrical conductivity was measured for 488 biochars produced in pilot plant and industrial pyrolysis systems. As known from literature, SEC of carbonaceous powders depends strongly on measurement conditions, which must be precisely defined to ensure comparability. For the presented setup, biochars should be milled to a median particle size (d_{50}) between 25–150 µm and preferably measured under a compaction pressure of $\geq$ 62 MPa, which minimizes the influence of particle size relative to the effect of carbon speciation. The reproducibility of SEC measurements on a given sample was $<$ 4–6%, and operator-to-operator variability $<$ 3%. Biochars produced at 400 °C to 900 °C predominantly are semi-conductive carbons with SECs between 10^{-6} and 10^{4} mS cm^{-1}, increasing exponentially with pyrolysis temperature. Consequently, SEC correlated well with the hydrogen to carbon molar ratio, which is a widely used parameter to estimate biochar aromaticity and the mean residence time of biochar in soil. The presented method provides a simple tool to approximate carbon speciation and is highly sensitive in monitoring biochar quality and batch homogeneity.

1. Introduction

Biochar is a carbonaceous material produced by the pyrolysis of biomass and is considered for carbon sequestration when, e.g., applied to soil or materials [1]. It consists of condensed aromatic structures that contain delocalized π-electrons, which allow for electrical conduction, similar to materials like graphite, graphene, or carbon black [2]. Literature indicates that an increase in the crystallographic graphitic structure of the carbon atoms leads to an increase in their electrical conductivity [2]. This refers to an increase in aromatic condensation, which can be achieved by increasing the highest treatment temperature (HTT) during pyrolysis [3]. Hence, quantification of the solid-state electrical conductivity of biochar (SEC) could be used as a predictor of biochar's carbon speciation. Moreover, measuring SEC may assess the suitability of a given biochar as a (semi-) conductive material for future industrial applications. Further, SEC measurements could be used as a method for biochar quality control directly at industrial pyrolysis plants, as SEC reacts very sensitively to temperature changes during pyrolysis [4]. In contrast to many other methods available for characterizing carbon speciation in biochars, such as nuclear magnetic resonance spectroscopy, high resolution transmission electron microscopy, the benzene polycarboxylic acid method and hydropyrolysis, the SEC measurement can be carried out with comparatively little effort and without the use of chemicals, even outside a typical laboratory

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environment. However, so far, quantification of SEC has not been frequently performed to characterize biochar. Therefore, this study presents a simple and reproducible method to quantify SEC of powdered biochar samples, which has recently been added to the analytical guidelines of the European Biochar Certificate (EBC) [5]. Quantification of SEC should not be confused with the long-established approach for measuring salt content of biochar, namely the quantification of the electrical conductivity of an aqueous biochar suspension.

The SEC of carbonaceous powders can be quantified with a two-piston method [6–8]. The method involves compaction of the sample at a defined pressure between two pistons, which simultaneously act as electrodes, and measures the electrical resistance through the sample after applying an external current [9]. Improvements of this method, known as the guard cell method, have been established to distinguish between the surface and volume resistance of the compacted sample [9]. The latter is being considered as most relevant to estimate the electrical behavior of carbons in composite materials [9]. In the present study, however, we chose the two-piston method, as it is simpler to use in industry and therefore has been more widely used to characterize carbonaceous powders [6,7,10,11].

It is well known that the compaction pressure and particle size of carbonaceous materials affect the SEC in two-piston setups [6,12]. In earlier studies, compaction pressures have been mostly varied between 0.1–10 MPa [6,7,10,11]. Bartoli *et al.* applied a pressure up to 150 MPa to their biochar samples, however, they did not investigated the influence of the biochar particle size [13]. Celzard *et al.* proposed that a pressure of 1 MPa is high enough to achieve good electrical contact between the particles, however, they did not define particle sizes or crushing procedures, too. It is worthwhile to mention that Celzard et al. only used highly conductive carbonaceous samples like graphite, graphene, or activated bio-based carbons. In contrast, industrially produced biochars are made across HTT's spanning from 400 °C to 900 °C, resulting in a wide range of SECs, which could necessitate the use of higher measurement pressures [4].

The method developed for the EBC currently applies five different pressure steps in the range of 31 to 156 MPa [5]. The use of such high pressures allows the SEC measurement of biochar produced in the abovementioned range of HTT. As the method could serve as proxy for biochar carbon speciation and persistence in soil [4], the influence of other physicochemical properties on SEC measurement, such as particle size, should be minimized and accounted for. Since the range of pressures used in the present study is significantly higher than that applied in recent studies, the effects of pressure and particle size on SEC are revisited here.

Compared to previous studies on biochar SEC [8,10,13], the present work focuses on (i) defining a standardized measurement protocol that allows comparable SEC quantification across the wide range of HTT used in industrial biochar production, including quantification of its analytical reproducibility, (ii) providing a large SEC dataset of 488 biochars, including 402 industrial samples certified under the EBC scheme, and (iii) demonstrating the use of SEC as a highly sensitive parameter for monitoring within-batch homogeneity in industrial pyrolysis.

2. Materials and methods

2.1. Biochars

Biochars were either produced at pilot-plant or industrial scale. Feedstock, HTT, and pyrolysis technology of all biochar samples, as well as raw data on elemental analysis and SEC is available in the supplemental spreadsheet (S1 Table). At the pilot-plant scale, a PYREKA research pyrolysis unit (Pyreg GmbH, Dörth, Germany [14]) was used to produce three different sets of biochars. *Set A* included the sequential production of biochars from softwood or straw pellets in a range of HTT from 400 to 800 °C (50 °C temperature increments for HTT 400–600 °C, 20 °C increments starting from a HTT of 600 °C) with a residence time (RT) of 10 minutes. Data on *set A* were partly presented in an earlier study [4]. *Set B* included the production of biochar from beech wood or straw pellets at HTT ranging from 400 °C to 900 °C and RTs of 10–30 minutes. *Set C* included the production of two biochars from forest wood pellets, either at 700 °C or 800 °C and a RT of 10 minutes. All biochars are referred to below using abbreviations including the feedstock type, HTT, the corresponding data set, and sample identifier as listed in the supplementary spreadsheet (S1 Table). The sample Wood-500_{A18}, for example, is a biochar made from wood in data set A with the sample ID 18, which was produced at a HTT of 500 °C.

Industrial biochars were produced by various pyrolysis systems registered under the EBC. In total, data from 402 individual biochars produced in the years 2022–2024 and submitted for batch certification analysis to Eurofins Umwelt Ost GmbH (Bobritzsch-Hilbersdorf, Germany) were used. The EBC certification process ensures representative sampling [5]. This set of biochars was labelled as *set D*. In addition, a pyrolysis experiment was performed on a P500 pyrolysis system (Pyreg GmbH, Dörth, Germany) operated by Sonnenerde GmbH (Riedlingsdorf, Austria) using a mixture of forest wood and composting screen overflow pyrolyzed at 650 °C with a RT of 20 minutes. Here, from a total of 2 m^3 biochar production, 30 non-representative specimens were taken by grab sampling (*set E*). Likewise, 10 grab samples were obtained from a 0.2 m^3 production batch of biochar produced from hop pellets after bitters extraction. Pyrolysis was performed on a pre-commercial TCR©-unit with 30 kg h^{-1} biomass input, a HTT of 750 °C (TCR30, [15], *set F*). Further, two commercially available wood-based biochars produced at industrial scale by CarbonCycle GmbH & Co. KG (Rieden, Germany) and AWN Buchen GmbH (Buchen, Germany) were included in *set G*.

2.2. Drying and milling

Biochars from set D, E, F, and G were dried at 40 °C to mass constancy. All other biochars were sampled in dry condition from the pilot-plant pyrolysis unit and stored in air-tight plastic bags before milling. All biochars, except for *set D*, were milled to < 0.2 mm in an impact mill (PX-MFC 90 D, Kinematica AG, Malters, Switzerland). Biochars from *set D* were milled with a disc swing mill to < 0.2 mm by Eurofins Umwelt Ost GmbH. Additional biochars from set C were prepared by milling to $<$ 2 mm in an impact mill, a ball-mill for 20 min (PM-100, Retsch GmbH, Haan, Germany), or manually with mortar and pestle for two minutes to test the impact of particle size on SEC.

2.3. Reference materials

Four different reference materials were obtained in powder form and used as received: (1) a natural amorphous Graphite (article no. 7614.2, particle size $d_{85} = 75$ μm, 45–50% C, 50–55% ash) purchased from Carl Roth GmbH + Co. KG (Karlsruhe, Germany) labelled as "Graphite CR", (2) a graphene sample (article no 36LY.2, particle size ≤ 2 μm, thickness = 1–4 nm) purchased from Carl Roth labelled as "Graphene CR", (3) a carbon black called ENSACO® 250 (particle size ≤ 45 μm) purchased from Imerys S.A. (Paris, France) labelled as "Carbon Black", and (4) a graphite sample called TIMREX® KS75 (particle size $d_{50} = 23$ μm, bulk density = 0.24 $g\ cm^{-3}$, 0.07% ash) purchased from Imerys S.A labelled as "Graphite TR".

2.4. Quantification of SEC

Solid-state electrical conductivity was quantified on milled biochar samples using the Black Gauss Setup [16] under a pressure of 31, 62, 94, 125, and 156 MPa in a hydraulic press (Perkin Elmer, Waltham, MA, USA), which equals a load of 1, 2, 3, 4, and 5 tons on the scale of the hydraulic press (measurement cell displayed in S2 Fig.). The electrodes between which the biochar was compacted were connected to a digital multimeter in a 4-wire circuit (Type 2110-240, Keithley Corporation,

Solon, Ohio, USA; setup displayed in S3 Fig.). The resistance was measured in transverse direction through the sample. For each measurement, 1.40±0.02 g of biochar sample was poured into the measurement cell. Electrical resistance analysis was done directly after pressurization. The height of the biochar pellet inside the measurement cell was manually recorded to an accuracy of 0.25 mm on a scale attached to the piston of the measurement cell (S2 Fig.) prior to each subsequent step. The compact height was usually between 3 and 5 mm. Measurements of biochars belonging to set D were performed by Eurofins Umwelt Ost GmbH, while all other biochars were analyzed by the authors of this study.

The resistivity ρ (in Ω·mm) of the sample at room temperature was calculated using Eq. (1), where R is the electrical resistance measured by the multimeter (in Ω), A is the electrode surface (in mm^2), h is the height of the measuring cell including the sample under pressurization (in mm), and h_0 is the measurement cell height without a sample being inserted (=15 mm, constant for all measurement pressures). The electrode area A was calculated from its diameter d_e (=20 mm) according to Eq. (2). The SEC of the sample at room temperature was calculated according to Eq. (3) in mS cm^{-1} (millisiemens per centimeter).

$$\rho = R \cdot \left(\frac{A}{h - h_0} \right) \quad (1)$$

$$A = \frac{\pi}{4} \cdot d_e^2 \quad (2)$$

$$SEC = \frac{1}{\rho} \cdot 10^3 \quad (3)$$

The limit of detection (LOD) for SEC can be calculated for each individual biochar sample from Eqs. (1)-(3) using $R = 10^8$ Ω, which reflects the upper measurement limit for R with the multimeter, with the LOD depending on the net sample pellet height (h-h_0). The LOD was usually around 10^{-6} mS cm^{-1} for a given biochar.

The operator-to-operator variability of the method was assessed on a single biochar (Wood-775_{B70}) by three individuals. Each operator measured the sample in triplicates, from which an average SEC value was obtained for each operator. The variation coefficient of these three averaged values was defined as the operator-to-operator variability. For this experiment, in addition to the manual scale printed on the piston h and h_0 was determined using a caliper (Metav Werkzeuge GmbH, Emmerich, Germany) with digital display and 0.01 mm accuracy (S3 Fig.).

2.5. Elemental analysis and particle size distribution

Total carbon (C), organic carbon (C_{org}), hydrogen (H), nitrogen (N), sulfur (S), and ash content of biochars were quantified by Eurofins Umwelt Ost GmbH according to the analytical guidelines of the EBC [5]. Particle size distributions of milled biochars from set C were determined using an Analysette 22 NeXT laser particle sizer equipped with a wet dispersion unit (Fritsch GmbH, Idar-Oberstein, Germany). From the particle size sum distribution Q_3, the 10th, 50th, and 90th percentile (d_{10}, d_{50}, and d_{90}, respectively) was obtained.

2.6. Data analysis

All data analysis was performed in GraphPad Prism version 10.4.2 (Graphpad Software LLC, Boston, MA, USA). The decadic logarithm of SEC was correlated with the H/C_{org} molar ratio using a second order polynomial model and with the hydrogen content (w/w) using a linear model. Outliers identified by a built-in ROUT method were removed with a Q value set to 1.

3. Results and discussion

3.1. Influence of compaction pressure on solid-state electrical conductivity

Measured SEC values increased systematically with compaction pressure for any given biochar, regardless of its HTT or feedstock (Fig. 1). Still, saturation of SEC at increased pressure was indicated, which can be mathematically modelled by a restricted exponential function, i.e. a function describing a plateau of SEC with increasing pressure (S4 Table). Accordingly, SEC increases with the bulk density in the measurement cell for any given biochar (S5 Fig.). As compaction pressure increases, the contact between individual conductive biochar particles improves, thereby reducing contact resistance. This pressure dependency is well known from literature, where, however, the saturation of SEC occurred at significantly lower pressures (i.e., below 10 MPa). The lower pressure to achieve saturation is potentially due to the usage of much more conductive carbonaceous materials in the referenced literature [7,10,11]. For the tested set of biochars in the HTT range of 600–800 °C, SEC increased exponentially with HTT, which we presented in an earlier study [4].

3.2. Influence of particle size

With the different milling methods, the particle sizes of the two tested biochars were reduced to the range of 1 µm to 422 µm (based on d_{10} and d_{90} values, S8 and S9 Table). There were no substantial differences in biochar particle size after milling depending on the HTT. Median particle sizes d_{50} decreased in the following order for the two tested biochars: impact milling with 2 mm sieve (d_{50}=125–143 µm), hand-milling in mortar with pestle (d_{50}=80–83 µm), impact milling with 0.2 mm sieve (d_{50}=26–27 µm), and ball milling (d_{50}=4 µm, S6 and S7 Figs.). The influence of particle size on SEC was independent of the level of SEC; the latter being related predominantly to the HTT during pyrolysis (Fig. 2). Compared to the coarsest particle size fraction, ball milling to a median particle size of 4 µm reduced the SEC by 27–49% for a biochar produced at 700 °C and by 35–51% for a biochar produced at 800 °C, depending on the compaction pressure (Fig. 2). For median biochar particle sizes between 25 and 150 µm, i.e., the three coarsest fractions, SEC varied to only 2.8–5.6% for biochar produced at 700 °C and to only 1.5%−4.3% for biochar produced at 800 °C under pressures of 62 MPa to 156 MPa. Under 31 MPa compaction, the variation of SEC between these three coarser fractions was 9–10% for both biochars.

Decrease in conductivity, e.g. decrease of SEC with a reduction in particle size, might be explained by an increase in external surface area through milling by up to factor 33–38 for ball-milled samples compared to the coarsest impact-milled biochars (illustration in Fig. 2, under the assumption of spherical particles with average diameter = d_{50}). As a result, electrons must be transferred to a higher extent through the external surface of contacted biochar particles, which adds contact resistance to the whole particle consortium. This is in line with the lower resistivity of carbon filaments with higher particle diameters, as reported in literature [17]. Still, correcting SEC data for external surface area did not level out differences among the samples used in this study (S12 Fig.), indicating that additional, size-related geometric and physicochemical factors contribute. The size and connectivity of voids between individual particles, and thus the packing density achieved at a given compaction pressure, governs the conductivity network through which electrons move, and thereby the relative contribution of inter- vs. intra-particle resistance. For a given d_{50}, particle shape and aspect ratio further determine the number of contact points per unit volume and the effective contact area between particles. The role of residual moisture was minimized in this study by standardizing sample preparation: all biochars were dried at 40 °C to mass constancy prior to milling (Section 2.2), so that samples carried only hygroscopic moisture during SEC measurement. A systematic, mechanistic decomposition of these effects was beyond the scope of the present study and would require dedicated

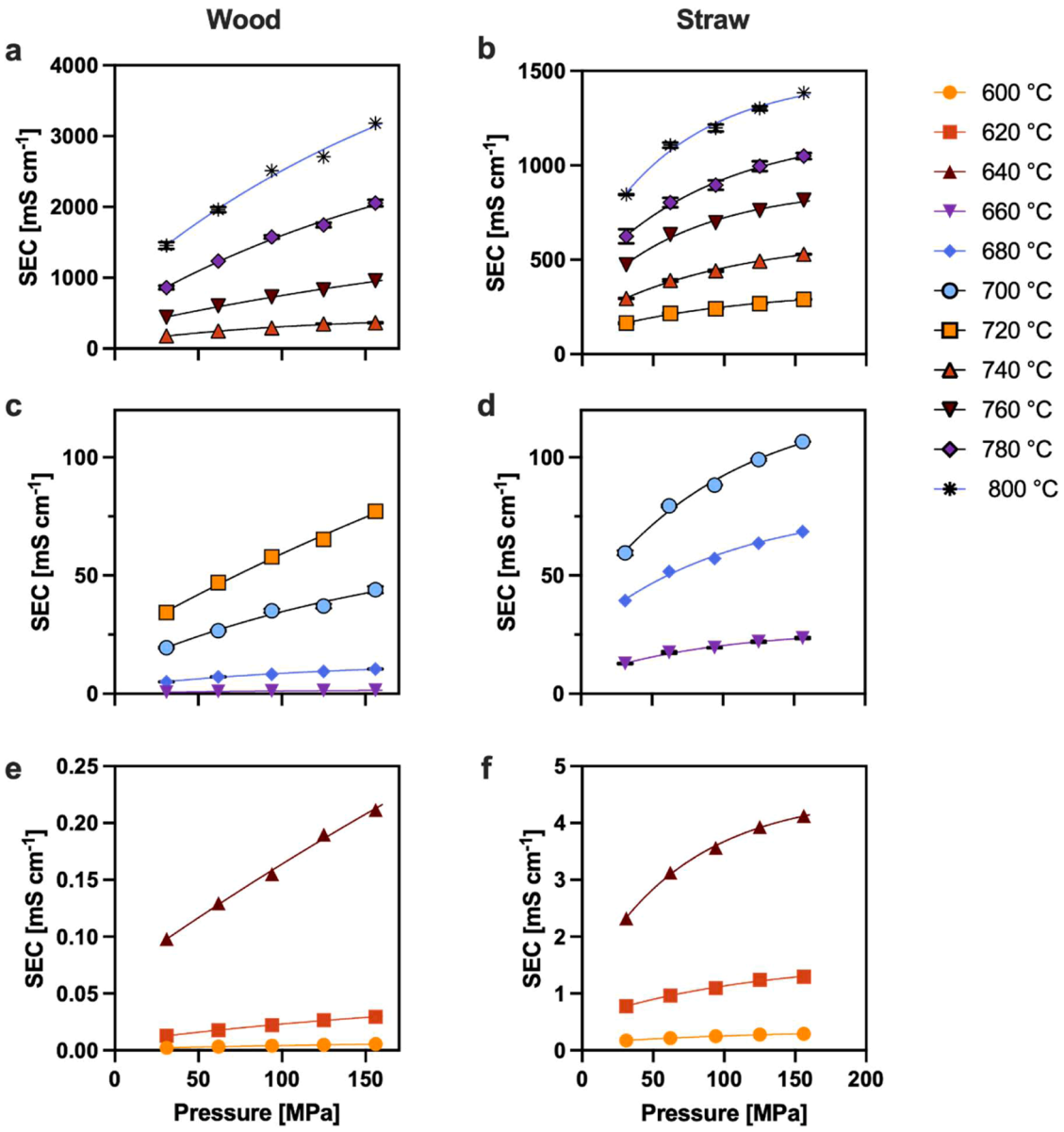

Fig. 1. Solid-state electrical conductivity (SEC) of biochar powders at different compaction pressures. Biochars were produced either from wood (a, c, e) or straw (b, d, f) pellets at pyrolysis temperatures between 600–800 °C and belong to data set A (S1 Table). The data per feedstock type are split into different panels representing different ranges of pyrolysis temperatures and SEC. The lines correspond to the restricted exponential model fitted to the data according to S4 Table. Biochars were milled in an impact mill with 0.2 mm sieve size, the mean particle size (d_{50}) is around 25 μm.

experiments with controlled variation of particle shape, packing geometry, moisture state, and also pore size and volume. Still, recommendations for optimum particle size ranges can be given based on the experiments presented in this study (cf. Section 5).

The relation between SEC and compaction pressure of the different median particle sizes (d_{50}) and biochars is presented in S13 Fig. and not further discussed at this point.

3.3. Methodological reproducibility

The variation coefficient for SEC resulting from triplicate measurements of six different biochar samples was below 6%, mostly below 4%, irrespective of the feedstock material (i.e., straw or wood), the level of SEC, and the compaction pressure (Fig. 3a, multiple data points for an individual sample represent different compaction pressures between 31 and 156 MPa). These samples were milled with the impact mill to <0.2 mm to an approximated d_{50} of 25 μm.

The operator-to-operator variability of the method could be reduced from < 6.2% to < 2.6% when a caliper with digital reading was used to determine the height of the compressed biochar in the measurement cell (Figs. 3b and S3). The measured values, either obtained by reading the height on the manual scale or with the caliper, matched each other to 91–95%. The SEC obtained by using the caliper was always lower, which can be explained by the difference in resolution of the two measurement methods. Even though this observation applies only to the Black Gauss device, these data highlight the importance of precisely determining the sample height in two-piston setups.

3.4. Contextualization of electrical conductivity of biochars with other carbonaceous materials

Biochars produced in a temperature range of 400 to 900 °C by slow pyrolysis on a pilot-plant scale had SECs between 10^{-6} and 10^{5} mS cm^{-1} (Fig. 4). Only two wood-based biochars produced at 400 °C were

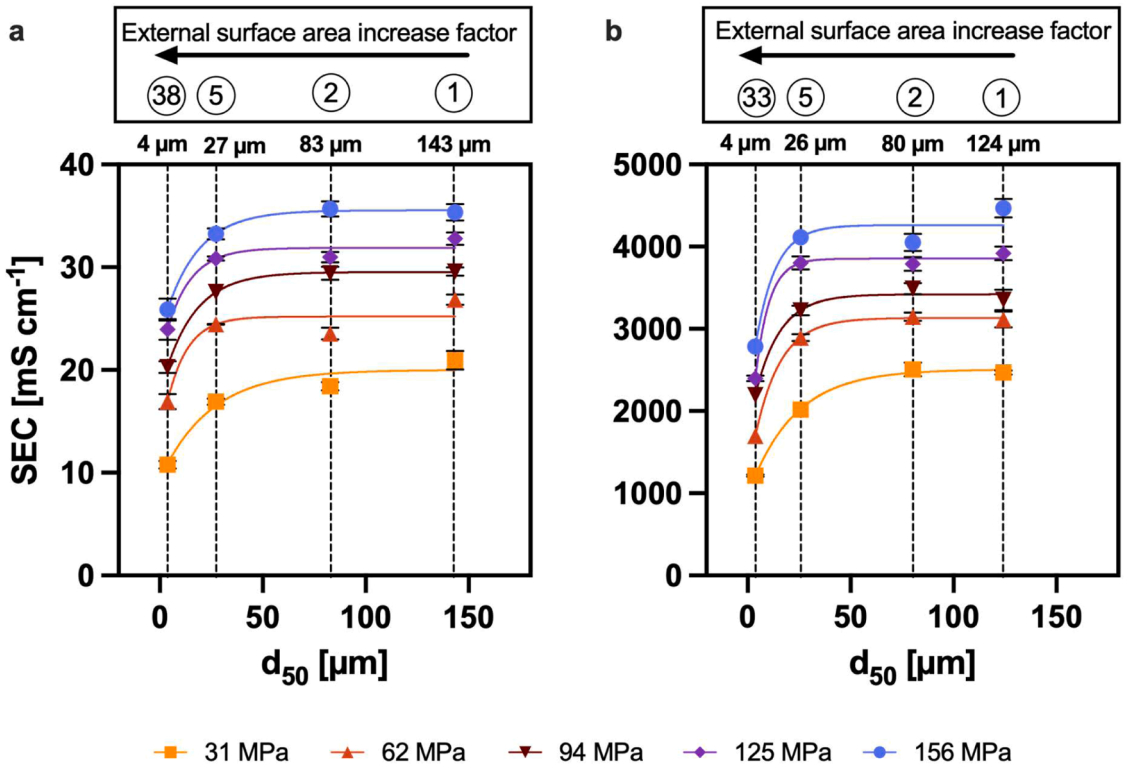

Fig. 2. Solid-state electrical conductivity (SEC) of wood biochars produced at 700 °C (a) or 800 °C (b) under 31–156 MPa compaction pressure (samples Wood-$700_{C88–91}$ and Wood-$800_{C95–98}$). Solid-state electrical conductivity is plotted against the 50th percentile of particle size sum distribution (d_{50}, values indicated above vertical dashed lines) after milling of biochars with different milling techniques, providing decreasing d_{50} values in the following order: impact milling with a 2 mm sieve (d_{50}=124–143 µm), mortar and pestle (d_{50} = 80–83 µm), impact milling with a 0.2 mm sieve (d_{50}=26–27 µm), and ball milling (d_{50} = 4 µm). Particle size distributions are presented in S6 and S7 Figs., as well as S8 and S9 Tables in the Supplementary Material. Numbers in spheres indicate the external surface area increase factor relative to the sample with the highest d_{50} in each panel (assuming a particle consortium with spherical particles and an average diameter equal to d_{50}). Solid lines represent a restricted exponential model fitted to the experimental data, parameters can be found in S10 and S11 Tables.

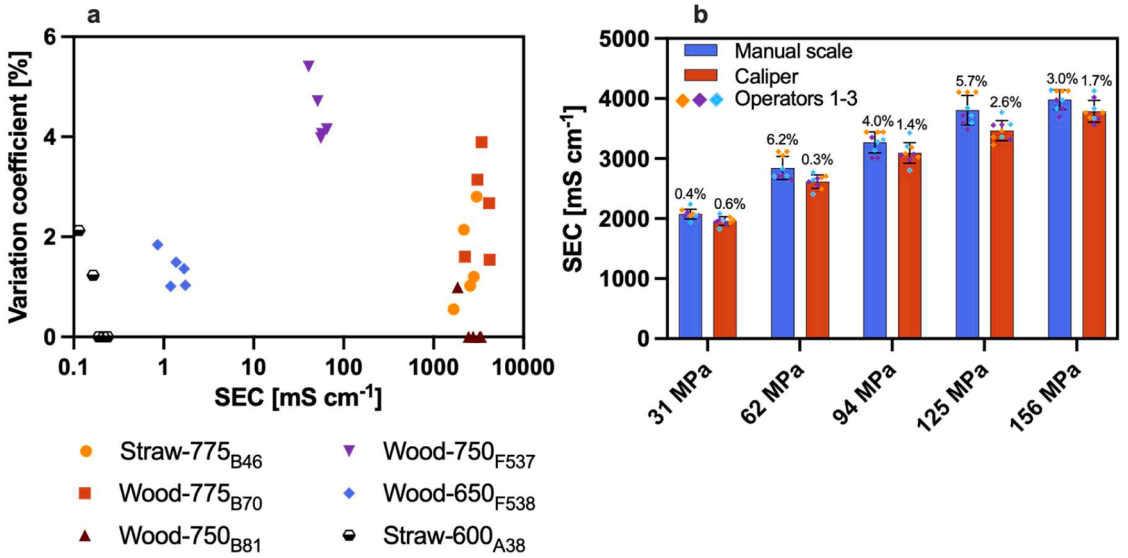

Fig. 3. (a) Variation coefficient of triplicate measurements by one operator of solid-state electrical conductivity (SEC) of six biochars made from straw or wood at the indicated pyrolysis temperatures (data set according to index) measured under five different compactions (31–156 MPa). (b) SEC of a powdered beech wood biochar produced at 775 °C (Wood-775_{B70}) measured in triplicates under the indicated pressure by three individual operators, which either used the manual scale printed on the device or a caliper to measure the biochar pellet height. Error bars indicate the standard deviation of the measured SEC across all operators (n = 9). Symbols indicate individual SEC measurements (different color for each operator). The percent value above error bars represents the variation coefficient of the three average SEC values reported by each operator, i.e., the operator-to-operator variability.

classified as isolators with a SEC below 10^{-5} mS cm^{-1}, while all other biochars were semi-conductive carbons (10^{-5} mS cm^{-1}< SEC <10^{5} mS cm^{-1} [18]). A total of 342 industrially produced biochars analyzed for EBC certification covered the spectrum of SECs equal to biochars

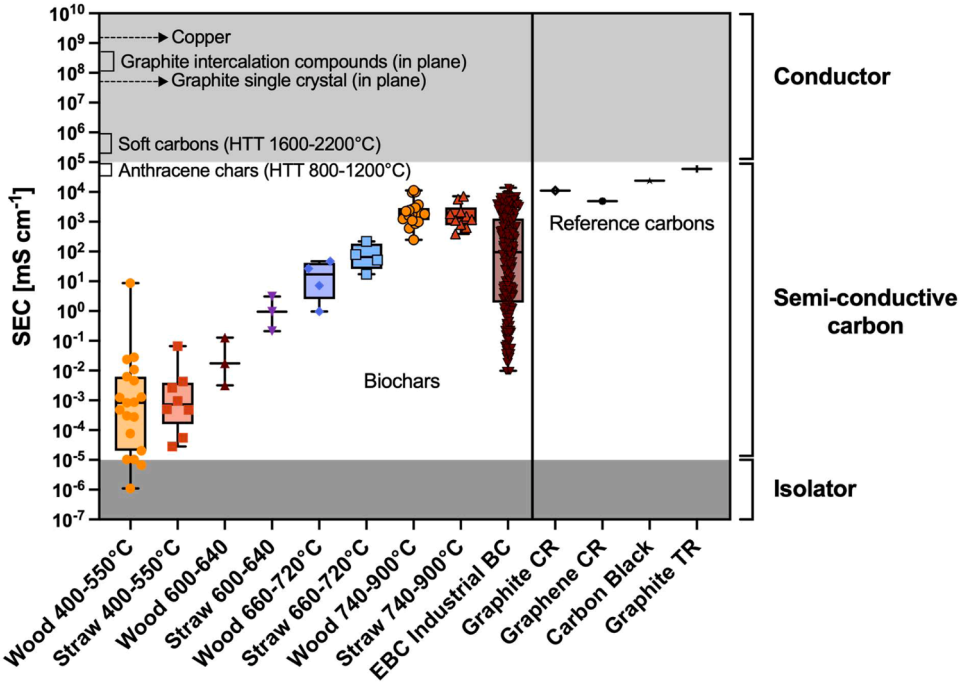

Fig. 4. Solid-state electrical conductivity (SEC) of biochars produced on pilot-plant scale (set A and B) sorted by biomass type (wood or straw) and highest treatment temperature (HTT). Biochars registered in the European Biochar Certificate (EBC) in the years 2022–2024 are presented separately (n = 340) with SEC ≥ 0.01 mS cm^{-1} (*set D*). In this set, an additional 69 industrial biochars had lower SEC, which was reported as < 0.01 mS cm^{-1} by Eurofins Umwelt Ost GmbH, these samples are therefore not presented. Measurements were performed under 62 MPa compaction pressure. Boxes represent the 25th to 75th percentiles and whiskers indicate the range of minimum to maximum of measured values, which are presented individually by symbols. Horizontal lines in boxes represent the median value. Reference values of other carbon types and copper indicated at the ordinate are based on literature [2]. In addition, average values of SEC of four measured reference materials are shown in individual columns: two natural graphites (from Carl Roth – CR or Timrex – TR), graphene from CR, and a commercial carbon black. Indicated ranges for isolators, semiconductors, and conductors are based on literature [18].

produced on pilot-plant scale at a HTT between 550 °C and 900 °C, which matches well with the pyrolysis systems and the associated range of HTT used in industrial biochar production [19]. Additional 69 industrially produced biochar samples were analyzed with a SEC being below the quantification limit of <0.01 mS cm^{-1} set by the commercial laboratory for practical reasons, which are therefore not presented in Fig. 4. The actual LOD with the applied multimeter, however, is 10^{-6} mS cm^{-1} (cf. Section 2.4). As there is no known pyrolysis system for biochar production operated below 400 °C [19], the SEC of these remaining 69 industrially produced biochars is assumed to be between 10^{-6} and 10^{-2} mS cm^{-1}, based on the observations from pilot-plant pyrolysis.

Not only the HTT, but also the RT and reactor load, i.e., the mass flow of biomass through the reactor, might impact the intensity of pyrolysis and, with that, the degree of aromatic condensation in biochar and its SEC [20,21]. The variability in SEC observed for pilot-plant biochars in the temperature range of 400–550 °C can be attributed to differences in RT, reactor load, and the movement of feedstock in the reactor. Here, a biochar produced at 525 °C with a long RT of 30 minutes and a low reactor load had a significantly higher SEC (Fig. 4), while most other biochars in this set were produced at lower HTT, with RT of 10 minutes and higher reactor load.

In general, biochars' SEC range includes that of two carbon allotropes, depending on the HTT. Biochars produced at 500–525 °C had SEC values around 10^{-3} mS cm^{-1} (Fig. 4, S1 Table), similar to that observed for the Fullerene allotrope (Table 1). Biochars produced at HTT > 740 °C with a minimum RT of 10 minutes had SEC values in the range of 10^{2}–10^{4} mS cm^{-1} (Fig. 4), a range typically observed for carbon blacks (Table 1), indicating that they might be replaced by ecologically more sustainable alternatives such as biochar.

The SEC of the four different reference materials was in the range of 5000–59,000 mS cm^{-1} and increased in the following order: Graphene CR (5000 mS cm^{-1}), Graphite CR (11,200 mS cm^{-1}), Carbon Black (23,900 mS cm^{-1}), and Graphite TR (59,000 mS cm^{-1}, Fig. 4). Lower SEC quantified for graphene compared to graphite and carbon black was observed in a similar measurement setup [7], which is generally unexpected based on literature values (Table 1). The reason for the comparably low SEC quantified for graphene is likely due to the measurement electrical conductivity in the transverse direction through the sample, while graphene commonly has high in-plane conductivity of up to 22•10^{7} mS cm^{-1} [22], which is largely ineffective in the present setup. Similarly, electrical conductivity of graphite varies depending on whether it is measured within the basal plane or the perpendicular prismatic plane (Table 1) [23]. In our setup, graphite particles might have arranged disordered in the measurement cell, which could explain the quantified SEC of the two samples lying in between literature values for the basal (10^{6} –10^{7} mS cm^{-1}) and prismatic plane (10^{3} mS cm^{-1}, Table 1). Differences in SEC between the two graphite samples might be related to differences in crystallinity, impurities, or geological history [23]. Conductivity measurements of the four reference materials confirmed the plausibility of our setup, yielding values consistent with

Table 1
Range of electrical conductivity of various carbon allotropes and carbon forms. Values were retrieved from literature, except for biochars, which are based on the current study.

Carbon Allotrope / Form	Electrical conductivity [mS cm^{-1}]
Biochars	10^{-6}–10^{5}
Fullerene [24]	10^{-3}
Carbon Black [24]	10^{2}–10^{4}
Graphite (prismatic plane) [23]	10^{3}
Graphite (basal plane) [23,24]	10^{6}–10^{7}
Carbon nanotubes [24]	10^{7}–10^{8}
Graphene (in plane) [22,24]	10^{8}–10^{9}

those reported for similar carbonaceous samples using a comparable method [7].

3.5. Correlation of SEC with biochar elemental composition

To understand relationships of SEC and other biochar properties across the large sample set presented in this study, correlations with the elemental composition of all biochars were tested. This analysis was not separated by feedstock type. The vast majority (> 90%) of industrial biochar produced under EBC is from woody biomass. A detailed query and assignment of the feedstock to the analysis data was not promising and beyond scope due to the low proportion of non-woody biomass.

The decadic logarithm of SEC correlates with the H/C molar ratio of biochars using a quadratic model (Fig. 5a), which was also found for a data set from literature [10]. Still, a large range of SEC for a given H/C ratio was observed, especially for H/C molar ratios between 0.2 and 0.4, where SEC varied by up to four orders of magnitude for a given ratio (Fig. 5a). Differences in aromatic condensation, which are not reflected by H/C molar ratios, might be responsible for this observation. The exponential increase in SEC with HTT and the corresponding quadratic decrease in log(SEC) with H/C molar ratio are consistent with the established three-stage model of pyrogenic carbon condensation [3,25,26]. At low HTT, biochar consists of hydrogen-rich, partially aromatic structures with limited π-electron delocalization. With increasing HTT, polyaromatic clusters grow at the expense of aliphatic and oxygenated moieties, leading to a steep decline in H/C and a steep increase in π-electron density and SEC. At HTT > ~700 °C, inter-cluster alignment into turbostratic, graphene-like domains progressively reduces the activation energy for inter-cluster electron hopping, approaching the SEC of carbon blacks [3,25,26]. The SEC dataset presented here can thus be interpreted as a high-throughput, low-cost proxy of these structural changes. Further, SEC negatively correlated with the hydrogen content of biochars (Fig. 5a), but no correlation was identified with other tested properties such as carbon content, ash content, and content of polycyclic aromatic hydrocarbons (PAH, ∑16 EPA PAH, Fig. 5c, d, and f, respectively). Due to their π-electron system, PAH have electrical conductance, too, which increases with molecule size [27]. The absent correlation with PAH content supports that SEC in biochars is not an artefact from condensation of aromatic contaminants on the biochar. A linear decrease in SEC was found when a single biochar is mixed with ash or other mineral matter at increasing ratios, which acts as insulator in the biochar matrix (S15 Figure). This illustrates that SEC depends on the interaction of several properties of the biochar which is determined by both feedstock type and pyrolysis temperature. A mathematical combination as product of molar H/C ratio and ash content did, however, not correlate with SEC (Fig. 5e). This highlights that SEC of biochars

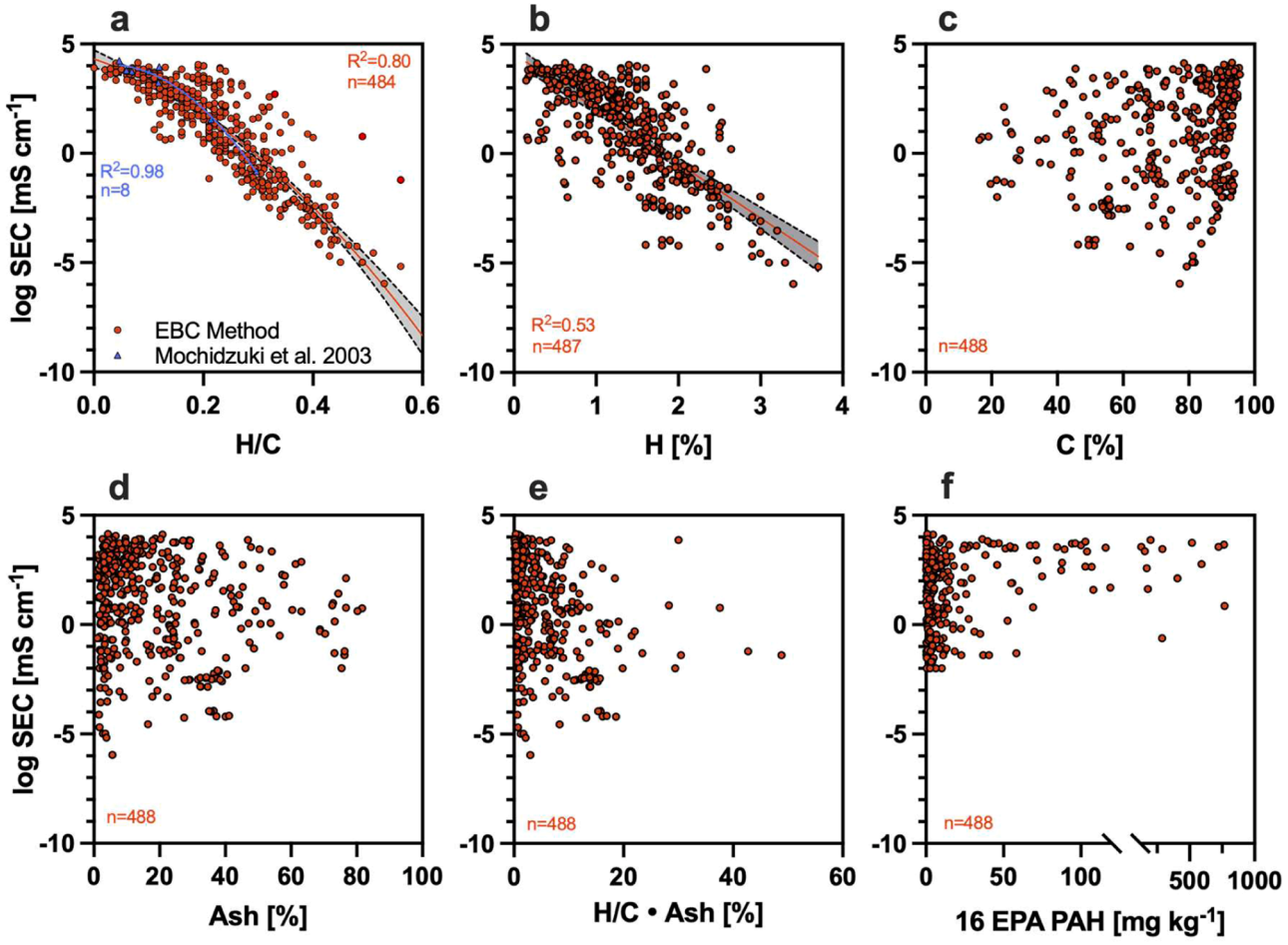

Fig. 5. Decadic logarithm of solid-state electrical conductivity (SEC, measured under 62 MPa) over hydrogen to carbon (H/C) molar ratio, hydrogen content, carbon content, ash content, product of H/C molar ratio and ash content, and content of polycyclic aromatic hydrocarbons (∑16 EPA PAH) of biochars either produced on pilot-plant or industrial scale in panels a-f (all biochars listed in supplemental spreadsheet). Where available, organic C values were used. Please note that the dataset is dominated by low-ash biochar (median 12% w/w, mean 20 ± 20% w/w). The solid lines represent the fitted models (quadratic model in panel a, linear model in panel b) obtained for measurements performed with the method from the European Biochar Certificate (EBC). Here, the grey filled area represents the 99% confidence bands. In addition, data from Mochidzuki et al. [10] is presented in panel a, which was measured at 7.6 MPa for eight biochars, and is also fitted to a quadratic model. Quadratic model in (a): $\log(SEC) = (4.3 - 8.6 \cdot H/C_{org} - 21.0 \cdot (H/C_{org})^2)$ mS cm^{-1}. Linear model in (b): $\log(SEC) = (-2.5 \cdot H + 5.6)$ mS cm^{-1}.

might not only be dependent on process parameters of pyrolysis and elemental composition of the feedstock, i.e. ash and carbon content, but might also be influenced by other biomass properties such as lignin, hemicellulose and cellulose contents, which needs further investigation. In general, the combination of SEC data and structural characterization methods like Raman and Nuclear Magnetic Resonance spectroscopy as well as High-Resolution Transmission Electron Microscopy would be valuable in follow-up studies to attribute SEC causally to the underlying chemical composition, the degree of crystallinity, and the atomic arrangement of the carbon matrix in biochars.

4. Prospects for application of SEC measurements in biochar quality management

The strong linkage of SEC and HTT could be used in biochar production to identify potential system malfunctions, i.e., insufficient heat transfer in the reactor. This is highlighted by the comparison of SEC, carbon content, and H/C molar ratio of samples deliberately taken in a non-representative way from two biochar batches produced under industrial relevant pyrolysis conditions (Fig. 6). Samples presented in Fig. 6a–c were taken from a 2 m^3 production batch of a P500 (Pyreg GmbH), and samples presented in Fig. 6d–f from a 0.2 m^3 production batch of a TCR30 (Fraunhofer UMSICHT). While the C content and H/C molar ratio only varied slightly across non-representative subsamples taken from these two biochar batches (< 10 %, Fig. 6), the variation coefficients for SEC were between 260% and 290%. From this, it can be concluded that SEC is a highly sensitive parameter allowing for the distinction between individual biochars, which would not be possible by the other parameters presented. Online or inline measurement of SEC at the biochar output of industrial pyrolysis systems could thus represent a valuable tool to assess pyrolysis process stationarity. Therefore, an initial application of the SEC method could be quality assurance in the production of biochar using consistent feedstock within a pyrolysis unit.

In addition, knowledge of the SEC of biochars could help to approximate the electric conductivity of biochar-based, synthetic composites, which might be interesting in the future to replace composites based on fossil fuel-derived carbon blacks [13].

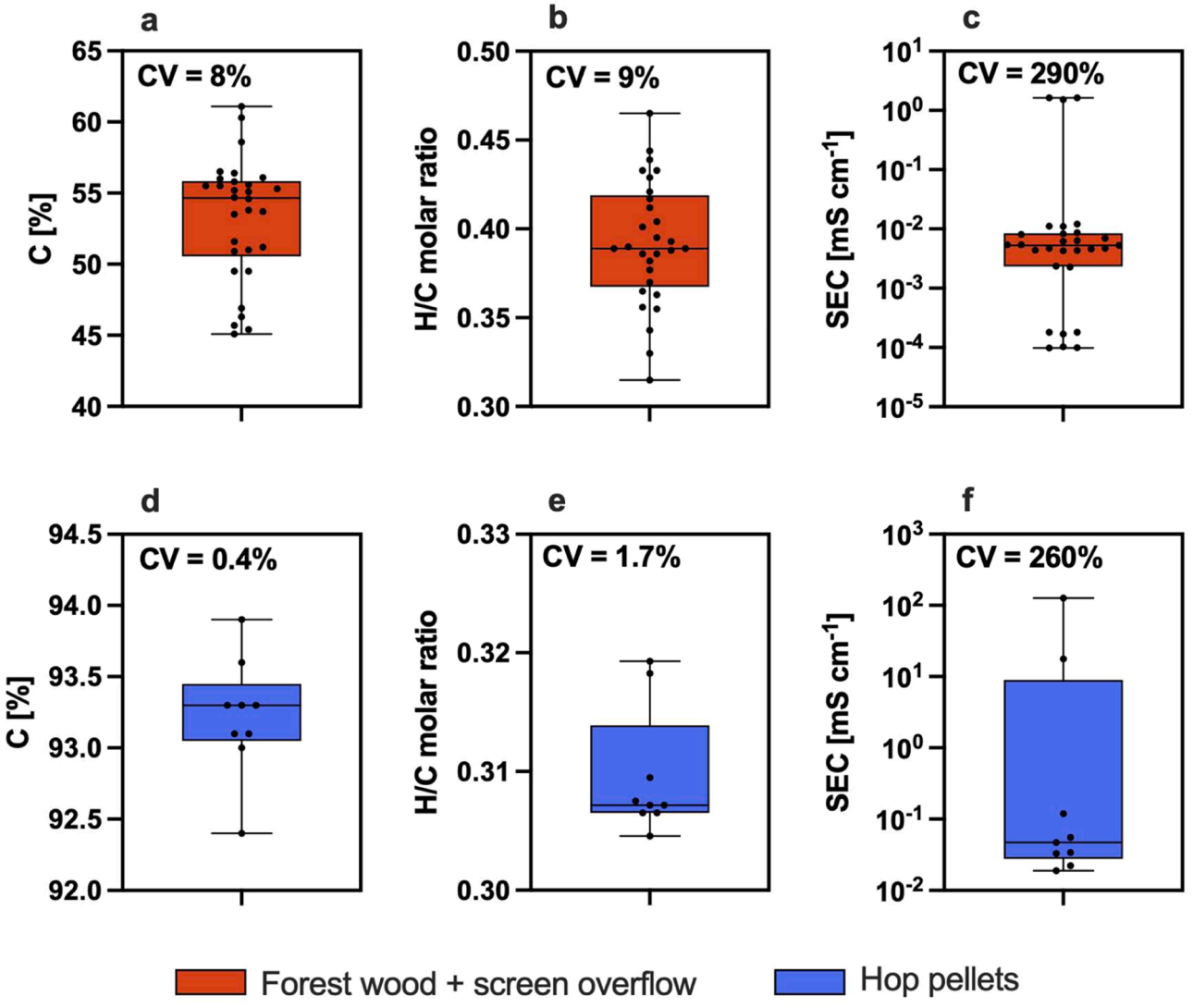

Fig. 6. Carbon (C) content, hydrogen to C molar ratio (H/C), and solid-state electrical conductivity (SEC, measured under 62 MPa) of grab samples from two biochar batches produced either from a mixture of forest wood and composting screen overflow residues on a P500 at 650 °C (Pyreg GmbH, Dörth, Germany, panels a-c, n = 30, set E) or from hop pellets on a TCR30 at 750 °C (Fraunhofer UMSICHT, Sulzbach-Rosenberg, Germany, panels d-f, n = 9, *set F*). Coefficients of variation (CV) are presented within panels for each parameter. The solid line of box plots represents the median value, error bars indicate the range of minimum to maximum values, and symbols represent individual data points.

5. Methodological recommendations to practitioners

To minimize the influence of particle size on SEC measurements, based on Section 3.2, biochars should be milled to a median particle size of 25–150 μm and subjected to a measurement pressure of ≥ 62 MPa (equal to a weight load of 2 t on the Black Gauß). Ball milling to fine powders is not recommended for sample preparation, as it substantially reduces the SEC of biochars. If the aforementioned pressure cannot be achieved, a median particle size of 25–150 μm under a measurement pressure of 31 MPa can minimize the influence of particle size on SEC to an acceptable extent. Measurement pressures should always be reported. Particle sizes larger than $d_{50} = 150$ μm were not tested, as they would not be of practical interest anyway, since milling is a prerequisite for obtaining representative aliquots of a given biochar sample in the lab. For pressurization, a laboratory hydraulic press, commonly used for the preparation of KBr pellets for infrared spectroscopy, is recommended for use with the presented setup, as it allows easy variation of compaction pressure. Alternatively, pressure could also be applied with a toggle press that delivers a constant force, usually available with a maximum of 12 kN force provision, which equals 38 MPa in the Black Gauß setup, i.e., within the range of the lowest pressure applied in this study.

To increase the method accuracy and reduce person-to-person variation, the height of the biochar compact should be measured using a digital caliper with 0.01 mm accuracy (cf. Section 3.3).

6. Conclusion

This study successfully established a simple and reproducible method for quantifying the SEC of biochar. The use of a two-piston "Black Gauss" setup, which is commercially available, ensures that results can be easily compared across different studies and laboratories. Our findings confirm that both compaction pressure and particle size significantly influence the measured SEC. The proposed standardized protocol yielded high reproducibility, with operator-to-operator and measurement variability below 6%.

It was demonstrated that SEC is a reliable proxy for pyrolysis conditions and biochar properties, which increases exponentially with HTT for a given feedstock and correlates strongly with the H/C molar ratio across different feedstocks, a key indicator of biochar aromaticity and recalcitrance in soil. This suggests that SEC quantification can be used as a simple, low-cost tool to estimate carbon speciation. Still, as our biochar set was dominated by biochars rather low in ash content (20±20% with a median value of 12%, w/w), the model presented here to predict H/C molar ratios based on SEC should be refined by including further ash-rich biochars. Since electrical conductivity generally decreases with increasing ash content, it is not clear whether SEC can still inform on carbon speciation at very high ash contents (e.g., > 50% w/w). To facilitate the use of SEC data, we suggest presenting it in logarithmic form, so that, for example, for a wood biochar produced at 400 °C, data would be reported as log(SEC) = −5.9 and for a HTT of 800 °C as log (SEC) = 3.4.

Quantification of SEC could be used for quality control and process monitoring in industrial biochar production, helping to identify system malfunctions like insufficient heat transfer. Furthermore, the electrical conductivity of biochars produced at elevated temperatures (in our case 740–900 °C) approaches that of commercial carbon blacks, highlighting their potential as sustainable alternatives to fossil fuel-derived materials for various industrial applications.

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CRediT authorship contribution statement

Jannis Grafmüller: Writing – review & editing, Writing – original draft, Visualization, Investigation, Formal analysis, Data curation. **Nikolas Hagemann:** Writing – review & editing, Supervision, Methodology, Formal analysis, Data curation, Conceptualization. **Frank Clemens:** Writing – review & editing. **Thomas D. Bucheli:** Writing – review & editing, Resources. **Viola Bartsch:** Investigation, Data curation. **Daniel Kray:** Resources, Investigation, Data curation. **Stephanie Spahr:** Writing – review & editing, Resources, Investigation. **Martin Meiller:** Writing – review & editing, Resources. **Hans-Peter Schmidt:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Hans-Peter Schmidt reports a relationship with Carbon Standards International AG that includes: board membership. Hans-Peter Schmidt and Nikolas Hagemann are authors of the Carbon Standards AG guidelines for the certification of biochar quality assurance (EBC) and biochar-based carbon sinks (EBC C-Sink / Global Biochar C-Sink, Global Artisan C-Sink). If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cartre.2026.100662.

Data availability

Data is available in the manuscript and the supporting information.

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