

REVIEW

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Black (pyrogenic) carbon in soils and waters: a fragile data basis extensively interpreted

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Abstract

Black (pyrogenic) carbon (BC) has its origin in incomplete combustion of organic matter. It is considered to be a stable fraction of soil organic carbon (SOC) accounting for a great proportion of SOC in many soils. The aim of this article is to verify the reliability of the three most widely applied methods to determine BC in soils: the benzene polycarboxylic acid (BPCA) method, the UV/NMR method and the ^{13}C NMR method. All these methods strongly overestimate BC in soil and dissolved BC in waters. The main reason for the overestimation can be attributed to the fact that these three methods measure the polycyclic aromatic carbon (PAC) present in BC. However, PAC structures are also a component of humic substances so that a part of humic C is measured as BC. It can be concluded that the importance of BC in soil and waters is strongly overestimated and should be critically reevaluated.

Keywords: Black (pyrogenic) carbon, Humic substances, Black carbon overestimation, Biochar, Soil organic carbon

Introduction

Today there is no consensus within the scientific community about the chemical forms of stable soil organic carbon (SOC) and about the mechanisms of preservation, reactions, and degradation of SOC, partly due to the complexity of forms and reactions in soil including chemical, biochemical, and biological reactions and partly due to the different points of view under which soil organic matter (SOM) is considered, e.g., soil fertility, or soil as a C sink or source.

High concentrations of SOC may be a main origin of soil fertility. The relation between SOC concentrations and soil fertility is not positive over the whole range of SOC concentrations since peaty soils may be less fertile than mineral soils with relatively high SOC concentrations. The effect of soil organic matter (SOM) on soil fertility strongly depends on the chemical forms of soil organic carbon [1]. Two developments in SOM research within the last three decades can be observed: an increasing focus on the biology of soil organic matter transformations, and the introduction of fire-affected (pyrogenic or black) carbon (BC) as an assumed main component of stable soil organic matter. Both drifts are accompanied

by a reduced interest in soil humic substances chemistry and biochemistry or even by an attitude to ignore soil humic substances [2].

Both BC and humic substances are considered to constitute stable SOC pools in soils. This is of central relevance considering elevated CO_2 levels in the atmosphere, which may be partly compensated by accumulation of organic carbon within stable soil fractions.

In this paper, a critical reevaluation of the methods and results of BC determination and quantification in soils and dissolved BC (DBC) in waters is presented, and conclusions are drawn with respect to the quantitative roles of BC and DBC in soils and waters, their possible contributions to climate changes mitigation, and the role of added BC/biochar application to improve soil fertility.

Gerke [3] already made some critical comments on the determination of BC in soils. The present paper is a strong extension including some important recent papers (Nakane et al. [4]; Zimmermann and Mitra [5]; Wagner et al. [6]) and especially Chang et al. [7] who showed that the most widely applied method to determine BC—the BPCA method—is not specific for BC.

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Black (pyrogenic) carbon in soil and its potential ecological relevance

Black or pyrogenic carbon (BC) as fire-affected organic matter has its origin in incomplete combustion [8] and is considered to be a stable part of soil organic carbon (SOC) with a potential to mitigate the increase of atmospheric CO₂ concentration [9].

The increasing importance of BC and of its manufactured form, biochar, within the scientific community is documented by Novotny et al. [10]. They counted the number of scientific articles on BC in the period between 2007 and 2014 and found an increase from 8500 to more than 18,000 papers a year till 2014. For biochar, the respective numbers were very low in 2007 and increased to about 880 papers in 2014. One conclusion of these results may be that the rising number of BC papers helped to increase the interest in biochar, as a technical application of some types of black carbon to soil.

The present high-level interest in BC and biochar application to soil probably has its origin in studies which showed high concentrations of BC in tropical soils up to 300 (mg BC/g SOC) with BC being 30% of SOC [11, 12]. In European chernozems, values between 15 and 45% were reported [13] and interpreted in such a way that “Black chernozemic soils in central Europe originate from ancient biomass burning” [14], suggesting that BC is the most important SOC fraction in chernozemic soils. In the US agricultural soils, Skjemstad et al. [15] detected BC contents up to 35% of SOC. All these values represent indeed relatively high and significant proportions of BC of SOC. In the same vein, Ponomarenko and Anderson [16] found high BC contents in Canadian chernozemic soils. However, those authors were more careful and wrote about an organic fraction resistant to UV irradiation which is similar to char.

From the above-cited papers, it may be concluded that BC is an important part of SOC in these fertile soils and thus, the application of biochar may be a technique to improve soil fertility in general.

Probably the above-cited papers have induced extensive research on BC in soil and subsequently on biochar as soil fertilizer.

However, the methods to determine BC in soil have to be critically reevaluated.

Gerke [3] described some critics with respect to the methods used for the determination of BC in soils. Three recent papers [4, 5, 7] now allow a conclusive description of the problems associated with the most common methods to determine BC in soils.

Quantitative determination of BC in soils—frequently used methods, pitfalls, and errors

After the publication of Schmidt et al. [17] who compared several common methods to determine BC in soils, a critical reevaluation of data and interpretation of BC in soils gained before was warranted. This is especially remarkable, because the main authors who found very high BC values in several soils also contributed to the comparative analysis by Schmidt et al. [17].

Schmidt et al. [17] compared six methods to determine BC in eight Australian soils, four of them including thermal oxidation of SOC by heating at temperatures ranging from 340 or 375 °C with or without preextraction and/or chemical preoxidation. The organic residue after thermal oxidation was attributed to be BC.

We here only compare the commonly used method with a maximum temperature of 375 °C including preextraction/oxidation (CTO 375) with two other methods. The CTO 375 method gave values up to 7.5 (mg BC/g SOC). [The 340 °C methods gave higher values between 7.0 and 23.4 (mg BC/g SOC) probably because not all of the non-BC was oxidized at lower temperatures]. The remaining two methods have been widely applied and delivered high BC values. The BPCA method after Glaser et al. [18] uses oxidation of SOC. The formed benzene polycarboxylic acids (BPCAs) are considered as a measure for BC in soil and are quantified by chromatographic methods. A factor then relates BPCA yield to BC content in soils.

Using the BPCA method, Schmidt et al. [17] found BC values in the same eight Australian soils between 37.2 and 131.1 (mg BC/g SOC), the BC values determined with BPCA methods being higher by a factor of 10–15 than the values determined with the CTA 375 method.

The last method in this comparison consists of a combination of oxidation of SOC by UV-irradiation and the determination of BC in the residues by solid ¹³C NMR spectroscopy assuming aryl C signals being distributed between lignin and BC [19]. The UV/NMR method gave the by far highest BC values in six of the eight Australian soils which were higher up to a factor of > 500 than the CTA 375 values [17].

The BC values determined by the CTA 375 method were the by far lowest values. However, there are two reasons, as to why BC values in soils may be overestimated even by the CTA 375 method:

1. Simpson and Hatcher [20] found that during the thermal treating, pyrogenic artifacts were produced which were then determined as BC.
2. Differential thermal gravimetric analysis showed that the main weight loss of charcoal during heating was > 400 °C, which was similar to lignin [21]. From these

data, it may be concluded that a part of soil lignin is determined as BC with the CTA 375 method. This fact may be the reason, why Edmondson et al. [22] differentiated BC in soil by differential thermogravimetric analysis, over the region between 200 and 470 °C attributing to “ecosystem-derived organic carbon” and the region between 470 and 600 °C attributing to BC.

In some cases, the BC values may be overestimated with the CTA 375 method, but the BPCA and the UV/NMR methods probably will strongly overestimate BC. This is the main result of the comparative study of Schmidt et al. [17].

The reasons for the overestimation of BC by the BPCA method now can clearly be described.

Brodowski et al. [23] showed that the BPCA method described by Glaser et al. [18] overestimates BC up to 90%. They attributed this failure to the HCl pretreatment which they substituted. Kappenberg et al. [24] showed for the modification of the BPCA method that only BPCA with penta- or hexacarboxylic acids should be used as markers for BC, and other BPCAs may originate from non-BC materials.

Glaser et al. [18] stated that they investigated, during the development of the original BPCA method, whether humic substances can be oxidized to BPCAs during the oxidation process and came to the conclusion that humic substances do not interfere with the BC analysis. However, they did not investigate soil humic acids. Instead, they used polyphenol polymerization products from ground apple, Maillard reaction products from arginine and fructose, and relatively fresh incubation residue of barley straw. They did not investigate humic substances, from which it is known that they can be oxidized to BPCAs [25, 26]. During the development of the BPCA method, there was an urgent need to test whether BPCAs are formed from humic substances during the BC analysis. This was avoided by Glaser et al. [18]. Those authors defined some reaction products of straw and apples as representatives of soil humic substances. Without any experimental proof, they stated that humic substances do not interfere with the BC analysis (e.g., [11]).

The work—which Glaser et al. [18] avoided—was done by Chang et al. [7] in their excellent paper. They tested the BPCA method on three soil samples and for some materials including fulvic acid, humic acid, lignin, and humic acids extracted from the three soil samples. By means of sequential removal of organic carbon fractions in the soil samples, Chang et al. [7] showed that humic substances contributed between 71.8 and 82.6% to the BPCAs formed during analysis which was performed according to [23]. In the same soil, samples BC, as the

residual fraction in the extraction sequence, contributed between 2.4 and 10.1% to the BPCA formed. Chang et al. [7] also showed that humic acid from non-pyrogenic origin resulted in high BPCA activity after oxidation performed according to [23]. They simply showed for the three soil samples that after the extraction of humic substances with NaOH, the BPCA yield after oxidation was reduced to between 71 and 83% [7]. All these analytical procedures should have been conducted by Glaser et al. [18] during the development of the BPCA method to confirm a possible effect of soil humic substances on the BPCA yield.

Mature humic substances with polycyclic aromatic carbon (PAC) strongly contribute to the formation of BPCA [7]. Chang et al. [7] showed that mainly B5CA and B6CA substances were formed from humic substances, which is in contrast to the results of Kappenberg et al. [24] who recommended these BPCAs as indicators for BC. Chang et al. [7] concluded thus: “...The assignment of BPCAs to BC should be avoided.”

In their paper, Chang et al. [7] also found that fulvic acid and lignin showed low BPCA contents after oxidation. Bostick et al. [27] showed that compost, oak biomass, and grass biomass gave very low BPCA yields when using the method of Brodowski et al. [23]. Both results support the view that mature soil humic substances, and not fresh degradation products and newly formed SOC (humic precursors according to [28, 29]), show BPCA activity after oxidation.

We may conclude thus: measurements of BC in soil with the BPCA method in its variations will strongly overestimate BC if humic substances are present.

The UV/NMR method after Skjemstad et al. [19] also overestimates BC which may explain the extremely high BC values for this method in the comparative study to Schmidt et al. [17]. This may be due to only partial destruction of non-BC carbon in soil, mainly humic substances which were shown to be resistant to UV irradiation (e.g., [30] and references therein). Novotny et al. [10] formulated the same argument on the rejection of the UV/NMR method for the determination of soil BC as follows: “Removal ... of non-pyrogenic C depends on the oxidation intensity which is overall lowest in the case of photooxidation...”

It seems that the UV/NMR method to detect BC in soil had been abandoned after 2002 with the exception of a ring trial [31] where it was used probably for comparison purposes.

The scientific BC community is obviously aware of the overestimation of BC by the method of Skjemstad et al. [19] and the original BPCA method of Glaser et al. [18], at least after the publication of the papers of Schmidt et al. [17] and Brodowski et al. [23].

However, BC data collected with both methods are still used long time afterwards to emphasize the role of BC in soil (among others: [2, 14, 32–43]).

For example, Solomon et al. [38] wrote thus: "...biomass-derived BC seems the main precursors of these highly refractory polyaromatic structures. This conclusion concurs with the suggestions of ... Glaser et al. [11]." The values of Glaser et al. (here [11]) on BC contents of Amazonian soils were very high (>30% BC) mainly because of the use of the strongly BC overestimating method introduced by Glaser et al. [18]. A paper which summarized as a main result that highly refractory aryl-C is the key for chemical recalcitrance and assumed that the origin is from biomass-derived BC ignores the overestimation of their single reference for high BC-values in Amazonian dark earths, i.e., the paper of Glaser et al. [11]. And even 8 years later, Lehmann and Kleber [2] referred to Solomon et al. [38] by stating that thermally altered carbon from vegetation fires are found in most soils, are polyaromatic, and typically extractable in alkaline solution. Lehmann and Kleber could have known by 2015 that the BC contents in soils measured with the UV/NMR or the first version of the BPCA method after [18] are not reliable.

Meanwhile solid-state ^{13}C NMR has been used as a method to determine directly BC in soils. Aromatic C NMR signals are assigned to BC or lignin, and humic substances have been ignored for the quantitative interpretation of the NMR spectra [42–46]. However, aromatic C and PAC are present in soil humic substances [7, 25, 28, 47–52]. Some of the humic substances C will be determined as BC. Cusack et al. [42] gave an explanation for their procedure to ignore humic substances in soils: "Historically, humic material was thought to consist of large polymers containing aromatic compounds created via condensation reactions during microbial decomposition [1]. However the importance of the reactions and neoformation of super-molecules has been questioned [53]; recent analyses suggest that alkali-extractable SOC is dominated by biological molecules..."

This statement of Cusack et al. [42] is wrong for at least two reasons. First, humic substances as polymers are initially formed by polymerization reactions of mainly phenolic radicals, and condensation reactions may subsequently be important [3]. Second, a new view on humic substances is largely based on the work of Piccolo [54, 55] and his coworkers who postulated a supramolecular structure of humic substances. Piccolo et al. [56], Cozzolino and Piccolo [57], and Nuzzo and Piccolo [58] showed that the supramolecular structure could react to humic polymers by adding peroxidases or catalysts, indicating that sometimes or often the transformation of humic supramolecules to humic polymers is restricted

by the concentration of substrates (phenolic monomers) or catalysts (peroxidases, phenolases, OH^- radicals, or Mn, Fe) or both (see also [3]). Thus, Piccolo and coworkers emphasize the biochemical or chemical formation of humic substances in soil, too. To ignore humic substances in soil is not in the line with Sutton and Sposito [53] and Piccolo and coworkers. The direct determination of BC in soil by means of ^{13}C NMR spectroscopy assuming that no humic substances are present is not justified. Additional support for the rejection of ^{13}C NMR spectroscopy to determine soil BC comes from Zimmermann and Mitra [5]. They plotted the content of SOC against BC in soils and used the data of Reisser et al. [59] who conducted a literature-based inventory of pyrogenic carbon in soils. The linear correlation coefficient for the relation between BC weight and SOC weight was 0.93 for the determination of BC by ^{13}C NMR indicating a strong correlation between the two parameters. The correlation coefficient between BC and SOC for the BPCA method was also very high with 0.77. Zimmermann and Mitra [5] concluded for the BPCA and NMR methods as follows: "that these methods may have the greatest likelihood for artifacts that misidentify pyrC." Meanwhile ^{13}C NMR determination of BC in soil is used to calibrate BC determination by mid-infrared spectroscopy [60]. If, however, the calibration method is not reliable, then the determination of BC by MIR spectroscopy has no basis.

Waggoner et al. [61] showed by adding hydroxyl radicals, e.g., by Fenton reagent (FeII salt and H_2O_2) to lignin-generated polycyclic aromatic carbon species—this led DiDonato et al. [51] to the conclusion—that condensed aromatic compounds are a central part of soil humic substances. It, however, should be noted that Ziechmann ([28], p. 148–153) already described polycyclic aromatic structures in humic substances induced by hydroxyl radicals.

One conclusion is that with the aid of the most applied methods to determine BC in soil, the BPCA, the NMR, and the UV/NMR method, a more or less important proportion of soil humic substances, mainly polycyclic aromatic carbon, is determined as BC which will strongly overestimate BC in soil. It should be noted that in the CTO 375 method, no correlation between SOC and BC was found [5]. Reisser et al. [59] showed that the CTO 375 method yielded average BC values of about 5%, the BPCA method an average of about 10% of BC, and the NMR method and the UV/NMR method averages of about 15% of BC related to SOC. The determination of non-pyrogenic C in soil as BC is probably the reason for the close relation between BC and SOC, and among the soil organic C fractions, PAC as constituent humic substances may be preferentially determined as BC.

Black carbon and soil fertility—the role of biochar

The strong overestimations of BC by the BPCA, the NMR, and the UV/NMR methods may lead to an overestimation of the role of BC for soil fertility. From the experimental basis of high BC contents the increasing interest in biochar to improve soil fertility was derived. If fertile Amazonian soils, fertile European chernozemic soils and US agricultural soils exhibit high BC contents, then the application of biochar may improve fertility of many other soils (e.g., [10, 35, 62–64]).

The terra preta soil profile described by Glaser et al. [11] is not necessarily related to BC but may have its origin in the incorporation of high quantities of organic matter within restricted areas leading to an accumulation of nutrients and an increased formation of stable humic substances with PAC as component. The results of Chang et al. [7] strongly support such an interpretation.

The role of biochar application for soil fertility was recently reviewed by Jeffery et al. [64] by means of a meta-analysis. In temperate soils, the application of biochar depressed yield around 3% on average, whereas in tropical soils, yield was increased by biochar about 25% on average at median application rates of 30 t/ha or 15 t/ha to temperate or tropical soils, respectively. The effects of biochar on plant yield were both a liming effect and a nutritional effect. In a previous paper, Jeffery et al. [62] found also an increase of water-holding capacity which had a positive effect on plant yield besides liming effects and a nutrient effect of applied biochar. Considering their results of the meta-analysis, Jeffery et al. [64] summarized: “However in the light of this comprehensive analysis, the widespread hype of biochar use for crop yield effects must be questioned.”

The conclusion of Jeffery et al. [64] is not astonishing regarding the origin of the “hype”-false data on BC in fertile soils.

Three main problems concerning the effect of biochar on plant yield may be mentioned here:

1. Nutrient losses during the biochar production, e.g., of nitrogen should be considered.
2. In experiments which aim to quantitate the effect of biochar on plant yield, the question of the control is seldom discussed. The effect of the charred material on yield should be compared with composts produced from the same materials.
3. Possible toxic effects of biochar compounds, e.g., polycyclic aromatic hydrocarbons should be considered in more detail. The negative yield effect of biochar on soils of temperate regions as reported by Jeffery et al. [64] may be due to toxic effects.

The questions remain therefore whether or not the yield effects of biochar on tropical soils, the liming, and nutrient effects can be better achieved by calcareous materials and other fertilizers, e.g., composts or mineral fertilizers; and whether or not the water-holding capacity of soils can be better increased by compost from the same source which otherwise is pyrolyzed to biochar.

Biochar application to soil and the effect of BC on climate change

Another goal of biochar application to soil is to introduce stable organic carbon to mitigate the increase of atmospheric CO₂ concentration.

The problem associated with these considerations is that the actual concentrations of BC in soil are largely unknown due to the application of non-reliable methods for the BC determination, as described in the previous sections.

For example, Lorenz and Lal [9] reported soil concentrations up to 80% of BC, as related to SOC in surface soils. The cited source for this high value is Krull et al. [65] who, however, showed no such high value which instead probably comes from Preston and Schmidt [34] or Eckmeier et al. [37] who themselves reported this value citing the paper of Ponomarenko and Anderson [16]. However, all these cited authors described their data in such a way that up to 60% of organic C in soil and up to 80% in some soil fractions were resistant to UV irradiation and that the NMR spectra were consistent with the existence of char. Beside the already collected arguments questioning the determination of soil BC by the UV/NMR method, the citation of the results of Ponomarenko and Anderson [16] by Preston and Schmidt [34] and Eckmeier et al. [37] in their reviews is not justified.

If the BC content of soils is generally much lower than that is reported, then the persistence of BC may be lower than that is assumed, and it may be concluded that the application of biochar to soils must be reconsidered with respect to climate change mitigation even under the assumption that biochar added to soil reacts similar to soil BC. Lorenz and Lal [9] hypothesized that surface-applied biochar must be translocated to subsoil layers to achieve the storage of organic carbon for hundreds to thousands of years.

The experimental verification for such hypothesis requires accurate BC determination in soils which is obviously lacking.

Dissolved black carbon (DBC)

Black carbon losses from soil will probably reduce the BC stability and will decrease the ability of soils to represent a carbon sink via BC accumulation. The formation of dissolved black carbon (DBC) may lead to black

carbon leaching from soils at considerable rates as suggested by Jaffe et al. [66]. However, in their paper, the BC determination in waters was conducted after Dittmar [67] who used the BPCA method and, similar to Glaser et al. [18], ignored humic substances as potential interfering material for the analysis. Recently, Nakane et al. [4] showed that Suwannee River Humic acid II yielded a BPCA-carbon recovery between 5 and 6% supporting the role of river humic substances for the BC determination in waters by the BPCA analysis. The concentrations of humic substances in various rivers are high and accounted for between 50 and 80% of the dissolved organic carbon (e.g., [68–72]).

Wagner et al. [6] showed in their review on DBC a close relation between DBC and dissolved organic carbon (DOC). They explained this relation by the physicochemical affinity of both constituents to each other or/and by similar mechanisms of mobilization and stabilization for DBC and DOC. Similar arguments on the close relation between soil BC and SOC contents were put forth by Reisser et al. [59] and Zimmermann and Mitra [5]. Wagner et al. [6] described also a close relation between DBC and chromophoric DOC (CDOC) in arctic rivers which is aromatic rich. In another universe, this fraction may be named dissolved humic substances. However, Wagner et al. [6] did not even mention the possibility that CDOM is oxidized to BPCAs during the DBC analysis, which may have explained DBC values obtained in their review. For example, they reported that peat-influenced waters had high DOM concentrations and high DBC concentrations up to 2.8 (mg/l). Humic substances in peaty soils may account for 30% of peat dry matter ([48], p. 86) and may contribute to high DOM and DBC values in peat-affected waters. With the data on BPCA recovery of Suwannee humic acid II of 5–6% C [4] probably most of the BPCA-measured DBC can be explained by humic substances in Table 1 by Wagner et al. [6] assuming that dissolved organic carbon is similarly oxidized to BPCAs compared to the humic acid of Nakane et al. [4].

Interactions of humic substances and BC in soils

One simple assumption for the BC determination in soil by the reviewed chemical methods is that BC is relatively independent of other soil constituents.

Wagner et al. [73] proposed molecular structures for dissolved black carbon (DBC) which consists of various polycyclic aromatic carbon (PAC) molecules with varying contents of phenol, carbonyl, or carboxylic groups. The higher the contents of the latter groups the higher the water solubility of the BC molecules is. BC at the soil solid phase will possess a few of these hydrophilic groups which make the reaction with hydrophobic regions of soil humic substances more probable. Piccolo [54, 55] and

coworkers, and Piccolo and Conte [74] consider humic substances as relatively small molecules with a supramolecular structure stabilized mainly by hydrophobic forces thereby creating molecular associations of relatively high apparent molecular weight. The hydrophobic surfaces of the humic molecules adsorb, bind, and absorb BC into the humic framework. Simultaneously, BC may be bound to humic substances via metal bridges, mainly Fe(III) or Al(III) or electron donor–acceptor complexes ([3], Fig. 4).

The probable high affinity of soil BC to soil humic substances is relevant for the determination of BC in soils. Each of the methods to determine BC which were described above assume that no humic substances with polycyclic aromatic carbon exist in soil. The overestimation of soil BC following this wrong assumption is expected. If soil BC contents are relatively low, e.g., around some percent as suggested by the values of the CTA 375 method [59], then the question is that of the behavior of the soil humic substances incorporating BC and not of the BC as a single organic fraction in soils.

Conclusions

The most widely applied methods to determine black/pyrogenic carbon in soil (BPCA method, UV/NMR method ¹³C NMR spectroscopy) strongly overestimate black carbon in soils and dissolved black carbon in waters. The main reason for the overestimation is that polycyclic aromatic carbon as part of the humic substances is determined as black carbon. There is an urgent need to improve the determination of BC in soils and waters. The determination should consider the probable strong interaction between BC and humic substances or incorporation of BC into the humic frame.

Abbreviations

SOC: soil organic carbon; BC: black carbon; PAC: polycyclic aromatic carbon; BPCA: benzene polycarboxylic acid; DBC: dissolved black carbon; DOM: dissolved organic matter; DOC: dissolved organic carbon.

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