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Stable Carbon Compounds in Soils: Their Origin and Functions

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Abstract—The sources, formation conditions, and composition of stable carbon compounds in soils are considered in this review. It has been shown that the stable carbon compounds contain lithogenic carbon-containing components and pyrogenic material, as well as some stable compounds resulting from the biochemical transformation of biomass in the soil. The presented data indicate that pyrogenic components (black carbon) play the major role in the formation of stable carbon compounds in the soil; in most soils, the products of biomass combustion prevail over the technogenic emissions resulting from the combustion of fossil fuel. Methods for the separation and analysis of stable carbon compounds have been considered; the specificity of markers used for the diagnostics of carbon compounds of different genesis has been discussed. A tentative scheme has been proposed for the classification of carbon compounds in the soil depending on their genesis and stability. The contribution of black carbon to the development of soil morphology and properties has been discussed; the hypothesis about the deciding role of pyrogenic components in the formation of chernozem-like soils in Middle Europe has been challenged. The suitability of biocarbon application to soils for improving their properties and fixing carbon in the soil has been shown.

Keywords: carbon cycle, black carbon, biochar, pyrochar, hydrochar

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INTRODUCTION

Academician Dobrovolsky emphasized that the regulation of carbon cycle is one of the essential global functions of soils in the biosphere [6]; the transformation of organic substances and the residual accumulation of the most stable components with long specific lifetimes occur in the soil. Specific soil humic substances extractable by different solvents have been in the focus of researchers' attention for a long time [13]. Studies of stable black carbon compounds in the soil have been activated in the last years. This is in part related to the fact that the interest in carbon reserves and the carbon cycle resulted in an increasing attention to the most stable carbon compounds, which began to be considered as a final sink of carbon [108]. In addition, a boom in studies of biochar use as a fertilizer has been observed in the last years [23]. Along with soil carbon, many studies of stable carbon compounds are focused on the aerial [1, 59, 100] and aquatic [41] environments and bottom sediments [40, 70]; a few works deal with the transboundary transfer of carbon [89], including carbon and soot particles [12, 120]. These themes are considered in numerous works using different approaches and frequently different terminologies. As a result, the reader has problems with orientation in the forms of stable carbon compounds in soils, their origin, and functions in the soil profile and soil cover [91]. Therefore, it is worth investigating the terms and concepts related to stable carbon compounds, their position in the general system of carbon-containing substances in the soil, and methods of separating carbon compounds of different origins, as well as their role in the functioning of soils. The current review cannot be regarded as complete, because the works on the themes under consideration amount to hundreds or even thousands. Its aim was to outline the major problems related to the study of the most stable fraction of soil organic matter.

TERMS AND DEFINITIONS

First, we should define the concept of stable carbon compounds in the soil. The component of soil organic matter insoluble in alkalis or organic solvents, i.e., humin with approximately defined composition, is frequently considered a stable carbon compound [13]. However, the analysis of recent literature shows that the substances formally unconnected with soil organic matter but having some genetic relation to it should also be included in the list of soil carbon compounds. On the one hand, this is lithogenic carbon, i.e., components of sedimentary and metamorphic parent rocks: graphite, shungite, fossil coal, and kerogen. On the other hand, these are combustion products of biomass and fossil fuel, which are usually combined under the term of black carbon. There is no clear boundary between these groups of compounds. In particular, it was shown for marine sediments [40] that a significant part of inert carbonaceous products usually classified as black carbon contains almost no radiocarbon and, hence, results from the erosion of graphite schists rather than the combustion of organic fuel.

The term "black carbon" is differently defined in different disciplines and even different publications on the same discipline. The similar term "carbon black" (soot or technical carbon) is used in technical literature to define an industrial carbonaceous substance obtained in the pyrolysis or thermal oxidation of liquid or gaseous hydrocarbons [25]. It is used as a stabilizer of rubbers and polymers and a black dye [94]. These components, which are produced under controlled conditions, also get into the natural environment, including soils and sediments [127]; however, their amount is incomparable with that of technogenic compounds formed during the combustion of biomass and fossil fuel [70]. In the literature on soil science, technical carbon is almost not discussed. The term of black carbon initially referred to soot suspensions in the atmosphere. The interpretations of black carbon significantly vary between the atmospheric sciences and the soil sciences: atmospherologists take interest in all black particles absorbing the light, while soil scientists should separate black carbon from the other dark-colored products of the biochemical transformation of biological remains [55]. First of all, not only soot from the atmosphere gets into the soil, but also residual charcoal. Schmidt and Noack [108] propose to distinguish soot black carbon from char black carbon. The former results from the condensation of volatile combustion products and consists of various components including polycyclic aromatic hydrocarbons (PAHs) and graphite segments; the latter represents a residual phase formed during the pyrolysis and combustion of organic fuel. The spatial distributions of these components are obviously different: soot is transported to large distances, up to the Arctic ice [12, 22], while char substances are accumulated at the burning site. It should be noted that PAHs are permanent components of pyrogenic black carbon for both residual char and soot substances [3]. Along with lithogenic and pyrogenic carbon, the stable organic substance resulting from the biochemical transformation of biomass—which is partly associated with clay minerals (i.e., humin in the classical sense)—should also be considered [121].

In the soil, stable carbon compounds are found in a wide range of size and density fractions. Both kerogen and black carbon isolated from soils and sediments have characteristic particle sizes of several to more than hundreds of micrometers [116]. The morphology of particles can vary significantly: both rounded and angular particles are found; their surface can be smooth or profiled; amorphous aggregates can be found along with clearly defined particles [27]. The structure of soot black carbon has much in common with those of graphite and such natural material as shungite [9]. Onion-type structures observed in soot [108] almost repeat the structure of fullerenes [101].

The structure of pyrogenic products depends on the combustion temperature. Experimental study showed that chars can be grouped into four stages depending on combustion temperature in the range from 100 to 700°C: (i) transition char retaining the cell structure of plant material; (ii) amorphous char with randomly mixed heat-altered molecules and aromatic polycondensates; (iii) composite char consisting of poorly ordered graphene stacks embedded in amorphous phases; and (iv) turbostatic char dominated by disordered graphitic crystallites [62].

Kerogen and black carbon have low O : C and H : C atomic ratios [116]. The O : C atomic ratios for some plant residues, specific humic substances, and pyrogenic components are reported in the review by Brodowski et al. [27]; their values decrease with rising temperature: 0.4–0.6 for slightly charred wood, 0.2–0.4 for charcoal, and lower than 0.2 for soot. For soil humic substances, the ratio is 0.41–0.5. At the same time, Kramer et al. [71] note that highly carboxylated aromatic structures typical for black carbon have high content of oxygen and low content of hydrogen.

Appreciable amounts of nitrogen are present in stable carbon compounds [58]. The term "black nitrogen" was proposed to describe these nitrogen inclusions, which play an important role in the global nitrogen cycle [41].

IDENTIFICATION OF HIGH-TEMPERATURE CARBON PRODUCTS IN THE SOIL

The study of black carbon in soils involves two major issues. One of them is reduced to the assessment of the content of the above substances and their separation from the more labile amorphous components of soil organic matter. The other issue is the identification of the composition and structure of black carbon. Thermal and chemical analyses are the simplest and least expensive methods of estimating the content of black carbon in soils and sediments [47, 68]. Multi-element scanning thermal analysis showed that the major part of black carbon is oxidized in the temperature range from 550 to 750°C; organic matter of biochemical origin is oxidized at lower temperatures, and graphite at higher temperatures [58]. Soils of France were studied using the combustion of organic carbon at 375°C [29]; the residual phase was considered as black carbon, and its content was determined on a CHN analyzer. The authors noted that, under the pretreatment with hydrochloric acid for carbonate removal, some organic substances transformed to more thermally stable compounds; thus, the content of black carbon in calcareous soils can be overestimated. Song et al. [116]

proposed a procedure for the fractionation of soil organic matter, in which the residue nonhydrolyzable by sodium hydroxide (referred to as humin in Russia) is separated into kerogen, which is oxidized with a sulfochromic mixture (0.1 M $K_2Cr_2O_7 + H_2SO_4$, incubation at 55°C for 60 h), and black carbon, which forms the residual phase. Grossman and Ghosh [52] also recommended the sulfochromic mixture to be used for the separation of char material from the other soil organic matter. It should be noted that an earlier study showed partial oxidation of pyrogenic material by the sulfochromic mixture [114]. Another experimental oxidation of charcoal with the sulfochromic mixture showed that 28 to 40% of carbon was oxidized depending on the reaction time [67]. Gustafsson et al. [54] elaborated a protocol for the chemothermal analysis of pyrogenic carbon in soils and sediments, which includes the treatment with hydrochloric acid to remove carbonates, the thermal oxidation of organic nonpyrogenic carbon in the air in a tube furnace at 375°C, and the determination of the content of the remained black carbon in a conventional CHN analyzer at 1030°C. The authors showed that the content of radiocarbon in the residue remained before the last stage corresponded to that in the benzene polycarboxylic acids (BPCAs) used as a control sample [54]. BPCAs are considered as a sort of marker for black carbon of pyrogenic origin; their specificity for the combustion products of plant residues was first demonstrated by Glaser et al. [48]. Later on, this marker was repeatedly used for assessing the content of black carbon in soil organic matter [102]. The method of mid-infrared spectroscopy (8000–600 cm^{-1}) was also proposed for the rapid and inexpensive identification of BPCAs [26]. The infrared spectroscopy is a useful tool for the identification of the main components of soil organic matter, including black carbon [30]. Roth et al. [103] successfully applied the methods of mid-infrared spectroscopy and thermal and chemical oxidation for the separation of charcoal and soot in the soil, but they could not separate the pyrogenic components from the diagenetic carbon. However, the results of assessing the content of pyrogenic components from the present BPCAs are sometimes ambiguous, because it was shown that these compounds can be formed during the low-temperature incubation of plant residues, and isotopic studies showed that up to 25% of BPCAs in the natural soils can be of low-temperature origin [50].

The degradation of all components of soil organic matter, except black carbon, by photooxidation using ultraviolet radiation [115] was popular at one time; however, it was of little use later on, because the authors revealed its limited selectivity [109]. Schmidt et al. [109] examined some methods of thermal analysis and chemical extraction of black carbon: the comparison showed that their results are difficult to compare quantitatively, because the hard pretreatment decreases the content of residual carbon identified as black carbon. Simpson and Hatcher [113] showed that the widely used thermal methods could result in the formation of a residual phase similar to black carbon, even if the original samples contained no pyrogenic components.

In 2007, almost all world leading laboratories dealing with pyrogenic carbon performed a simultaneous determination of black carbon in laboratory and natural samples by 17 chemical, thermal, and combined methods [55]. A deplorable result was that each method extracted compounds from a specific region of the continuous range of pyrogenic transformation products of organic substances, from original organic products to soot. However, the work allowed the comparison and ranking of the methods used in different studies.

Some advanced versions of instrumental physicochemical methods, including Fourier transform ion cyclotron resonance mass spectrometry and cross-polarization magic angle spinning ^{13}C nuclear magnetic resonance, have been used for the identification of black carbon in the last few years [71]. These methods are able to identify highly carboxylated aromatic structures. In addition to these methods, Kaal et al. [61] used pyrolysis-gas chromatography and mass spectrometry, as well as thermally assisted hydrolysis and methylation, which made possible to isolate, in addition to permanent PAHs, such relatively simple components as benzene and toluene from the old (about 7000 years) charcoal in the soil.

SOURCES OF STABLE CARBON COMPOUNDS IN SOILS

The total volume of black carbon released to the atmosphere because of fires is estimated at 50 to 270 Tt [73]. Natural fires and technogenic waste formed during the combustion of wood and fossil fuel are generally considered the main sources of black carbon [4]. The natural sources primarily include forest fires [11, 51]; but fires in peatlands [8] and herbaceous ecosystems also contribute [39, 102]. Black carbon is well preserved in soils; therefore, it can be used in paleosol studies for the identification of forest fire conditions in the Pleistocene [125].

Forest fires result in the release of soot particles to the atmosphere and the formation of a sort of pyromorphic humus in the residual phase [51]. It was shown that the content of black carbon arriving into the soil with atmospheric fallout (soot carbon) is significantly lower than that of residual post-pyrogenic carbon [106]. The content and composition of pyrogenic PAHs in soils depend on the character of the burning material. Most polyarenes accumulate in soils after forest fires and combustion of coniferous plants; smaller amounts form after the combustion of herbaceous vegetation [5]. The diagnostics of pyrogenic or technogenic PAHs can be aggravated by the fact that these compounds not only get into the soil due to atmospheric transfer, but they also form in soils during biochemical processes [2]. However, the content of PAHs in the soils of the fire zone exceeds the background values by several times; in soils of the regions with wood combustion for municipal purposes, the difference reaches three orders of magnitude. It was shown that the content of PAHs in the areas adjacent to the fire sites is higher than at the fire sites themselves [17].

Along with the fires, the sources of black carbon in the soil include the technogenic emissions of soot caused by the combustion of fossil fuel like oil products [112] and coal [83]. The source of black carbon (combustion of biomass, coal, oil products, or other materials) can be determined from the morphology of soot particles or on the basis of chemical criteria such as the proportions of different PAH isomers [112].

Many human-transformed soils contain much pyrogenic material in both the occupational layer of settlements [72] and the arable soils, where there is coal due to slashing down [85] or targeted application [118]. The application of coal was practiced in some agrarian cultures, in particular in South America, where this resulted in the formation of peculiar dark-colored anthropogenic soils called terra preta do indio [77]. The use of biochar as a fertilizer is at its boom at present. Biochar results from the pyrolysis of plant residues at temperatures higher than 400°C under industrial conditions. The composition of biochar is variable and strongly depends on the temperature of its formation, which determines the O : C molar ratio in the resulting product [117].

Along with biochar (which is referred to as pyrochar by some authors), a similar product called hydrochar appeared recently, which is produced using a slightly different technology: plant residues are heated to 180–250°C in the presence of water [123]. Hydrochar contains more aliphatic components in its structure and is slightly less resistant to decomposition than pyrochar. In general, these products differ in composition and properties and can be considered as complementary to each other rather than alternative fertilizers [124].

As noted above, the pyrogenic nature of a part of black carbon can be in doubt, because BPCAs are not always reliable markers [50]. Andreeva et al. [21] found that the content of black carbon in some natural chernozemic soils of Buryatia is higher than in the analogous soils under long-term agricultural use; the authors concluded that the stable black carbon is of biochemical rather than pyrogenic origin and that it decomposes under plowing more rapidly than accumulates in the soil. Doubt increases because the content of black carbon increases in the soils to which organic fertilizers (manure) are applied [28]. The hypothesis about the low-temperature origin of substances analogous to black carbon is acceptable, because such reactions are permissible and described in classical works on organic chemistry [18].

There are many other sources of stable carbon compounds in soils. The recent urban soils contain particles of asphalt and coal tar that also get into black carbon [126], as well as much carbon compounds of lithogenic and diagenetic origin, which cannot be separate from the components of pyrogenic genesis [103]. The lithogenic sources include graphite schists [98], shungite schists [9, 15], carbonaceous and bituminous schists [104], and kerogen. Graphite and shungite are metamorphism products of organic and volcanogenic sedimentary rocks. Their difference is that shungite is the least ordered graphite form. Coals and bituminous schists mainly formed from peat during diagenesis and catagenesis. Kerogen, in a narrow sense, is a mixture of organic components of shale oils insoluble in organic solvents; in a wide sense, kerogen includes all the dispersed organic matter of sedimentary rocks [42]. Crude oil can obviously be considered as intermediate between the lithogenic and technogenic sources of carbon; the residual phase after its decomposition usually contains stable dark-colored compounds similar to black carbon [3].

STABILITY OF BLACK CARBON IN SOILS

In this review, we dwell on the stability of pyrogenic components, which apparently form the major part of the low-mobile fraction of soil organic matter. The stability of black carbon is estimated in different ways: some authors say that the black carbon resulting from the combustion of biomass is decomposed very slowly [81] or is almost indecomposable [51]; other authors show that it is successfully subjected to chemical [31, 32] and microbial [65, 90] oxidation. Kuzyakov et al. [74] found that the oxidation of charcoal in a model experiment proceeded extremely slowly, and the microbial oxidation was more active; however, 96% of the original substance remained unchanged. The comparison of the mineralization rates of black carbon under sterile and unsterile conditions showed that they differed insignificantly, which indicated no involvement of microbiota in the decomposition of char substances [24]. In Kenya, no reliable difference in the reserves or structure of black carbon was found between the plots of slash farming whose ages differed by 100 years [111]. In the Streletskaya Steppe (Kursk, Russia), the content of pyrogenic carbon in chernozem under fallow for 55 years decreased by 6%, while the content of total organic carbon in the soil decreased by 33% [119].

In the boreal zone, the slightly pyrogenically transformed components can be decomposed within a few tens and hundreds of years [99]. Lehmann et al. [78] used such modern techniques as scanning transmission X-ray microscopy with synchrotron radiation, and near-edge X-ray absorption fine structure spectroscopy and showed that, even after 1000 years of occurrence in the soil, the central part of a black carbon particle retained the strongly aromatic structure of the original char, and its peripheral part was enriched with carboxylic and phenolic compounds due to the oxidation of char and the sorption of humic substances from the environment. Cheng et al. [31] also confirmed using X-ray photoelectron spectroscopy that the oxidation of black carbon particles begins from their surface.

The supposition about the absolute stability of black carbon in soils is problematic, because its content significantly varies among soils, which is related to the differences in not only pyrogenic activity in different natural zones, but also water content [95], temperature [32, 96], physicochemical parameters of soils, their biological activities, and land use practices [37]. Farrell et al. [44] revealed an accelerated microbial mineralization of easily decomposable residual components during the three days after the application of biochar to the soil, which abruptly decelerated later on. Zimmermann et al. [129] performed an incubation experiment and showed that black carbon theoretically could decompose in the soil under tropical or subtropical conditions within less than a century; the authors confirmed that, during the decomposition of char, carbon dioxide released from the stable aromatic blocks rather than from the sorbed labile substances.

At the same time, Cheng et al. [33] showed that black carbon contains a fraction that remains stable regardless of climatic conditions. Hammes et al. [56], who compared the contents and compositions of black carbon in the modern chernozems from the Kamennaya Steppe and their samples taken in 1900, came to analogous conclusions. They found that the total content of black carbon in soils decreased by 25%; however, this decrease was due only to relatively low condensed substances, while the highly condensed aromatic compounds remained stable. Nguyen et al. [96] noted that the decomposition of the most resistant part of black carbon obtained at 600°C maximally depended on temperature. Zimmermann [128] showed in a model experiment that the half-life of biochar specially produced by pyrolysis varied from 10^2 to 10^7 years and related the decomposition rate with the temperature of char preparation: the chars produced at low temperatures (400°C), which contained the maximum amounts of aliphatic components, were most rapidly decomposed. Knicker [64] adhered to a slightly different opinion: he supposed that the relatively high decomposition rate of black carbon in soils compared to its theoretical values is related to the fundamental errors in the concept of black carbon nature. In his opinion, charcoal contains a heterogeneous mixture of biopolymers with relatively small polyaromatic fragments and numerous nitrogen-, oxygen-, and sulfur-containing functional groups rather than highly condensed polyaromatic compounds [64, 66].

In terms of the concept of carbon cycle, it is interesting to note that a part of the pyrogenic carbon in soils decomposes during new forest fires [105].

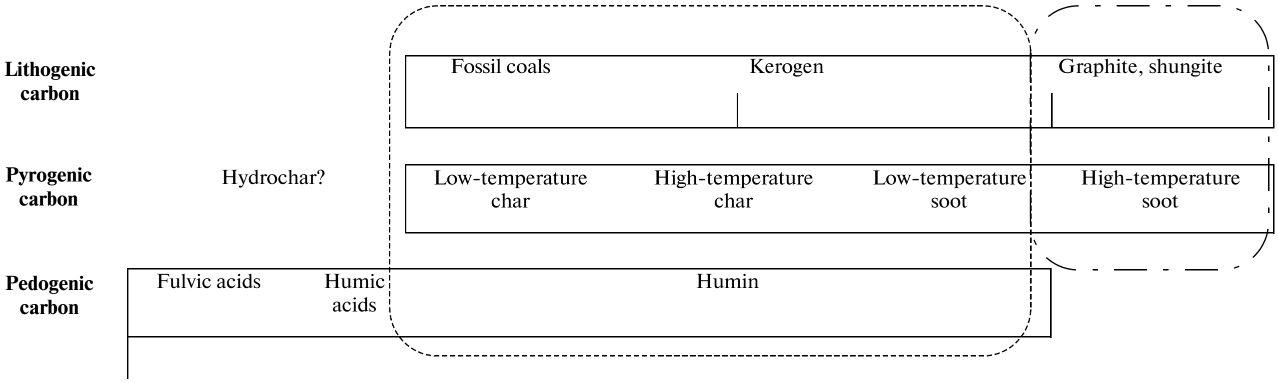
GENETIC AND SUBSTANTIVE CLASSIFICATION OF STABLE CARBON COMPOUNDS IN THE SOIL

The need of assessing the pools of organic carbon calls for the ordering of our knowledge of stable carbon compounds and the determination of their place in the general scheme of soil organic matter. We shall consider some partial classifications advanced earlier and propose a tentative general classification of organic matter in the soil. We specify that complex organic substances untypical for the soil (fresh plant and animal residues), carbon dioxide in the soil air, and solution, carbonates, and salts of low-molecular-weight organic acids (e.g., wheddellite, whewellite, and humboldtite) are not considered.

As noted above, the stable carbon compounds can be subdivided depending on their origin into lithogenic, pedogenic, and pyrogenic ones. This division partly reflects the temperature conditions of the formation of stable carbon compounds: the pedogenic compounds form at low temperatures, and the pyrogenic compounds at high temperatures. A similar fractionation scheme of organic matter [116] includes the separation into three components: humic acids, kerogen, and black carbon. In the classical Orlov scheme [13], the two last components obviously fall in the category of humin. The latter is the most stable humus component. It can include a significant portion of pyrogenic components. However, it should be kept in mind that this fraction also includes inert compounds resulting from biochemical reactions, as well as organic substances associated with clay minerals [121]. In our opinion, a general scheme for the structure of soil organic matter based on the unified principles is very difficult to develop. The main problem in the fractionation of organic matter by density, particle size, and solubility in different reagents is that it does not adequately reflect either the genesis of these components or their characteristic turnover time in the soil [86]. Therefore, we supposed that several parallel systems could be developed for substances of different genesis ranked by their stability instead of the unified scheme.

For example, the proper humus of biochemical origin can be described in terms of stability. The degrees of oxidation of different organic compounds are related to their stability: in particular, the more stable humic acids have a lower degree of oxidation than the relatively unstable fulvic acids [10]. However, it should be kept in mind that the resistance of organic components to chemical treatments does not always correspond to the stability of these components in the soil [90].

Masiello [91] proposed to subdivide black carbon by the degree of pyrogenic transformation of organic residues from slightly charred biomass to char, charcoal, soot, and graphitic black carbon. An important feature of this classification is the absence of sharp boundaries between different forms of pyrogenic material in soils and sediments.



Schematic diagram for the genesis and stability of carbon compounds in the soil: dashed lines delineate the groups of compounds of different genesis that are difficult to separate in practice.

For lithogenic carbon, a gradient of resistance to decomposition can also be determined. Based on the analyzed literature data, we proposed a general scheme presented in the figure. Dashed lines combine the substances of different genesis that are difficult to separate in practice.

ROLE OF BLACK CARBON IN THE GENESIS AND FUNCTIONING F SOILS

The limited size of this review makes it impossible to discuss the participation of lithogenic and pedogenic carbon in soil processes and soil fertility. We dwell on the review of concepts about the contribution of black carbon to the development of soils and their properties.

In aquatic sediments, the mean content of black carbon is 9% of the total carbon [69]. In soils, the contribution of presumably pyrogenic stable components is variable. Studies of organic carbon in soils of the steppe zone of Russia showed a significant proportion of black carbon: the authors estimated the content of pyrogenic components in chernozems at 17% of the total organic carbon [102]. In the savannas of the southern Great Plains (the United States), this value varied from 5 to 13% [39]. In the soils under Siberian taiga forests, the content of black carbon was 1.6–4.5% of the total soil carbon [38]; in the forest-tundra of the northern Middle Siberia, it was 0.6–3.0% [53]. In the plow horizons of German soils [28], the content of black carbon varied from 2.7 to 13.2% of the total carbon depending on the soil type; in the lower soil horizons, the absolute content of black carbon decreased, but its relative content increased up to 35% of the total carbon. According to the slightly different data of Schmidt et al. [110], black carbon made up 15 to 35% of organic carbon in the upper horizons of soils in Central Europe. The authors advanced a disputable hypothesis about the formation of dark-colored chernozem-like soils in Central Europe mainly due to the accumulation of pyrogenic black carbon [107, 110]. In their opinion, most of the Central European chernozems developed under woody plants due to slashing, while the common chernozemic soils should form under steppe vegetation [110]. The authors confirm their hypothesis by the presence of morphologically distinguishable char and soot particles. However, many questions remain without answers, e.g., the absence of thick dark-colored horizons under the taiga vegetation, where natural and artificial fires are prevalent no less than in the broad-leaved forests. In eastern Germany, the soils under pine forest contained a relatively large amount of microscopic char particles, which reflects repeated burnings [93]; however, no morphologically pronounced humus horizon was detected. In the podzols of northeastern Europe (Komi Republic), relatively small amounts of pyrogenic material accumulate in the forest litter and immediately under it [7, 43]. Moreover, it was shown recently that the statement about the coincidence of the area of Neolithic agriculture in Germany with the area of chernozemic soils [110] is not true [85]. It should be noted that the works of the Schmidt's team still need serious soil-genetic analysis.

The migration of black carbon with the downward water flow is insignificant: in a field experiment in the Colombia savanna (annual precipitation 2200 mm), only 1% of the added biochar migrated to depths of 15–30 cm during two years [88]. The formation of pyrogenic compounds is accompanied by the fixation of nitrogen in the form of stable compounds in some cases [92]. Organic material, including black carbon, usually interacts with the mineral soil component. A positive correlation was revealed between the contents of poorly structured allophane minerals and black carbon in soils of the Hawaiian Islands [36]. At the same time, the correlation between these components remained within the interaction of allophanes with soil organic matter as a whole.

Pyrogenic components can provide material for the condensed aromatic nuclei of humic acids in many soils [20, 57]. This is confirmed by the similarity of aromatic structural fragments in charcoal and humic substances according to the data of pyrolysis-gas chromatography and mass spectrometry, as well as thermally assisted hydrolysis and methylation [61]. Fokin earlier proposed a similar assembly model to explain the renewal of soil organic matter [16]. Later on, it was shown for some soils that biogenic humus physically separated from the pyrogenic nuclei contained extremely little polyaromatic structures; their content was even lower than in the original plant residues [75].

It is known that organic carbon in the soil under agricultural use is actively mineralized and released to the atmosphere; e.g., the loss of carbon from the chernozems of the steppe zone in Russia reaches 120 g C/m^2 in the first years of plowing [14]. The input of pyrogenic carbon into the soil significantly suppressed the soil respiration; i.e., soil organic matter was stabilized in the presence of black carbon [122].

As noted above, it is believed that black carbon in the soil participates in the long-term fixation of carbon from the atmosphere [112]. It was proposed to add biochar to the soil for fixing the carbon from the atmosphere [23, 46, 76]. Along with the fixation of carbon, biochar has a positive effect on soil productivity [117]: it caused a 189% increase in aboveground biomass production measured 5 months after the application [88]. It was shown that the fertility of many anthropogenic tropical soils, including Brazilian terra preta soils, was related to the liberal application of charcoal [49, 77]. Another positive effect of carbon material is that the stabilization of both original and added organic matter occurs in the soil in the presence of charcoal [82]; i.e., the mineralization rates of plant residues and humus decrease.

Experiments showed that the favorable effect of black carbon is related to the sorption of nutrients, which are usually leached from the poor tropical soils on its surface [77]. On the one hand, black carbon increases the cation exchange capacity of soils [80]; on the other hand, specific sorption of some organic compounds on black carbon is observed in soils and bottom sediments. It was shown that even low contents of black carbon in bottom sediments (0.3–0.6%) multiply increased the adsorption of such compounds as PAHs, polychlorinated dibenzo-*p*-dioxins, and polychlorinated biphenyls from the water environment [84]. Cornelissen et al. [35] showed that the adsorption of organic compounds by sediments and soils from water was higher than could be expected from the content of amorphous humic material by two orders of magnitude due to the presence of such components as black carbon, kerogen, and fossil coal, which are combined under the term of carbonaceous geosorbents. For PAHs, three adsorption mechanisms on black carbon are described: adsorption on surfaces, capture in micropores, and occlusion inside the black carbon structure [120]. It is interesting to note that humic and fulvic acids reduce the sorption capacity of char particles, because they block the inputs to their porous space [97].

The good sorption properties of biochar allowed it to be used as a sorbent for contaminants in soil and water. Biochar produced at a high temperature is usually used for the adsorption of organic pollutants because of the presence of large pores, and biochar produced at a low temperature is used for inorganic or polar organic compounds [19]. However, deterioration of the sorption properties of char introduced in the soil was noted with time: the sorption on the wood char that went into the soil in the 19th century was lower by 9–44% than on the fresh charcoal [34].

A favorable effect of biochar on the activity of soil microbiota was noted [79]. The mechanisms of this phenomenon are still not completely clear: this is obviously related to both the sorption of toxic metabolism products by biochar and the indirect increase in the content of nutrients in the soil. It is not very clear how these data agree with the results proving the stabilization of organic matter and the decrease of microbial respiration rate in the presence of pyrogenic organic matter [122]. In general, the chemical properties and effect of biochar on the productivity of soils are still being investigated. It was shown recently that biochar is a reducing agent in the soil [63]. Macdonald et al. [87] showed that the effect of biochar use depends on the type of soil: e.g., a positive effect was obtained for Ferralsols and Calcisols; no clear effect was observed for a Vertisol, and a negative effect was obtained for an Arenosol. Many hypotheses are based on short-term laboratory experiments, whose results are hard to extrapolate to actual production conditions; therefore, long-term and large-scale field experiments are required to reveal the acting mechanisms of black carbon in soils [60].

CONCLUSIONS

1. For the assessment of the balance and turnover of carbon on the Earth, it is important to consider its most stable forms, which are hardly subjected to chemical and biological destruction. These carbon forms include compounds of lithogenic, pyrogenic, and pedogenic origin.

2. Char and soot resulting from the combustion of biomass and fossil fuel are the major sources of stable carbon forms in the soil. However, the content of pyrogenic carbon in soils can be overestimated, because it is difficult to separate from lithogenic compounds or those resulting from biochemical reactions in the soil.

3. No reliable methods are still available for the fractionation of soil organic matter on the basis of genetic and even functional criteria. This is primarily related to the fact that carbon compounds form a continuum by genesis, composition, and properties.

4. In many anthropogenic soils, pyrogenic carbon determines the dark color and good sorption properties of the plow horizons. The hypothesis about the deciding role of black carbon in the development of

chernozem-like soils on vast areas in Europe is most probably invalid.

5. The pyrogenic carbon occasionally or intentionally introduced into the soil participates in the formation of soil humus, increases its stability, and favorably affects the ion-exchange properties of soils. In the last years, the application of biochar (pyrochar and hydrochar) found wide use for improving soil quality and binding atmospheric carbon. This is a recent practice, and many questions on the functioning mechanisms of carbonaceous substances in the soil remain.

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