

Editorial

Frontier Studies in Composition of Humic Substances and Soil Organic Matter

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Soil organic matter (SOM) is considered an integral component of soils and performs a multitude of crucial functions in the environment. The complexity of the molecular assembly inherent in humic substances (HSs) is reflected through their physical and chemical properties and creates opportunities for a broad range of interactions with both inorganic and organic components and living organisms. The wide variability of molecular composition of SOM and HSs, associated with their evolution under various environmental conditions, explains the challenges in their instrumental identification and the analytical detection of their molecular assembly macrostructure.

Therefore, our Special Issue was focus on “*Frontier Studies in Composition of Humic Substances and Soil Organic Matter*” and include novel research, reviews, and opinion pieces covering all related topics, including:

- (1) New approaches to the study of HSs and SOM;
- (2) Ecosystem functions of HSs and SOM;
- (3) Multiproxy study of HSs and SOM during the anthropogenic evolution of the environment;
- (4) Interaction of HSs with the organic and mineral components of soils;
- (5) HSs, animals, and humans (preparation of HSs used as feed additives for animals and food additives for humans);
- (6) Humic products: mechanisms of action, application, certification.

In “*Temperature Dependences of IR Spectra of Humic Substances of Brown Coal*” by D. S. Volkov, O. B. Rogova, and M. A. Proskurnin [1], the capabilities of temperature-monitored IR spectroscopy for studying the organic matter (OM) and mineral composition of HSs were tested. The authors found a reversible change in the frequencies of the band maxima in IR spectra upon heating, which they interpreted as forming structures with a particular order in the studied HSs in the dry state.

The second paper “*Organic Matter and Mineral Composition of Silicate Soils: FTIR Comparison Study by Photoacoustic, Diffuse Reflectance, and Attenuated Total Reflection Modalities*” [2] by the same authors is devoted to comparing photoacoustic, diffuse reflectance and attenuated total reflection FTIR modalities in the wide wavenumber range from NIR (7500 cm⁻¹) to FIR (150 cm⁻¹) for the same silicate soil samples under the same conditions; it was concluded that it is preferable to use all three modalities to characterize both SOM and mineral composition.

In “*Elemental and Molecular Composition of Humic Acids Isolated from Soils of Tallgrass Temperate Rainforests (Chernevaya taiga) by ¹H-¹³C HECTCOR NMR Spectroscopy*” [3], V. Polyakov, S. Loiko, G. Istigechev, A. Lapidus, and E. Abakumov studied humic acids (HAs) isolated from the soils of the Chernevaya and oligotrophic taiga in the Novosibirsk, Tomsk, Kemerovo, and Altai regions of Russia. They determined the structural and molecular composition of HAs, and the results demonstrated that the stabilization of organic compounds occurs in the soil of the Chernevaya taiga, which leads to the resistance of SOM to biodegradation that is not typical for benchmark soils of boreal environments.



Citation: Lodygin, E. Frontier Studies in Composition of Humic Substances and Soil Organic Matter. *Agronomy* **2023**, *13*, 188. <https://doi.org/10.3390/agronomy13010188>

Received: 23 December 2022

Accepted: 4 January 2023

Published: 6 January 2023



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The review article “*Carbon Polygons and Carbon Offsets: Current State, Key Challenges and Pedological Aspects*” by E. Abakumov and V. Polyakov [4] discusses the current issues surrounding the methods and methodology of carbon polygons and their pedological organization and function. The authors come to the conclusion that while creating the carbon polygon in any part of a country, we should discuss: (1) terminology; (2) the spatial coverage of Russia by polygons and the regional setting; (3) vertical frequency and temporal regularity of sampling; (4) how to store/process raw data and how to generalize the great data massive and (5) how the carbon unit itself depends on how to measure it and how to calculate it, and (6) whether the equivalent of the carbon currency will depend on our methodology and how we organize the network of carbon polygons.

The article by A. B. Volikov, N. V. Mareev, A. I. Konstantinov, A. A. Molodykh, S. V. Melnikova, A. E. Bazhanova, M. E. Gasanov, E. N. Nikolaev, A. Y. Zherebker, D. S. Volkov, M. V. Zykova, and I. V. Perminova titled “*Directed Synthesis of Humic and Fulvic Derivatives with Enhanced Antioxidant Properties*” [5] describes a directed modification of the humic backbone via incorporation of redox moieties for tuning up antioxidant properties of HSs. The results show, firstly, substantial difference in redox and antioxidant properties of the humic and fulvic acids, and, secondly, they can serve as experimental evidence that directed chemical modification of HSs can be used to tune and control antioxidant properties of natural HSs.

The article “*Effect of Pesticide and Humic Preparation on the Soil Structure during Pea and Chickpea Cultivation*” by O. Bezuglova, A. Gorovtsov, A. Grinko, S. Kartashev, A. Klimenko, V. Lykhman, E. Patrikeev, and E. Polienko [6] is focused the results of a 3-year experiment to study the soil structure with the combined use of insecticides and a humic preparation. The humic preparation BIO-Don10 was obtained according to the authors’ technology by alkaline extraction from vermicompost—a product of manure processing by compost worms of the *Eisenia foetida* species. According to the authors, the introduction of humic preparation BIO-Don10 into the technological scheme for the cultivation of legumes seems to be expedient both from the point of view of the economic effect of increasing the yield and also from the point of view of increasing soil fertility and preserving the agronomically valuable structure in it.

The purpose of “*The Role of Laccase from Zygomycetous Fungus *Mortierella elasson* in Humic Acids Degradation*” by A. Lisov, O. Belova, A. Zavarzina, A. Konstantinov, and A. Leontievsky [7] is to study the conditions of production of laccase by the fungus *Mortierella elasson*, to characterize the properties of the enzyme, and to evaluate its role in the transformation of HAs of different origin and composition. The results showed that laccase from a representative of zygomycete fungi can depolymerize HAs both in the liquid fungal culture and in vitro.

The variability of polycyclic aromatic hydrocarbons (PAHs) content across landscapes: pristine (the Hudson Mountains and the Haswell Archipelago), contaminated soils (stations Myrniy, Druzhnaya 4, and Bellinshausen) and unique samples of former agrosols transported by fly in-fly of polar staff from St. Petersburg, was determined in “*The Content of Polyarenes in Soils of Antarctica: Variability across Landscapes*” by E. Lodygin, E. Abakumov, and T. Nizamutdinov [8]. The statistical analysis of raw data allowed us to conclude that the contamination of pristine soils of Antarctica across variable landscapes is at the very initial stage. The data could be used as background levels for the elaboration of threshold concentrations of the PAHs for such an internationally managed region as Antarctica.

The objective of the paper “*Adsorption of Fulvic Acid and Water Extractable Soil Organic Matter on Kaolinite and Muscovite*” by K. Kolchanova, I. Tolpeshta, and Y. Izosimova [9] was to investigate the adsorption regularities of FAs and water-extractable organic matter (WEOM) isolated from horizon H of peaty-podzolic-gleyic soil on kaolinite and muscovite. The results showed that hydrophobic interactions on siloxane surfaces are the main mechanism to fix FA on both minerals. Kaolinite adsorbs slightly more organic carbon per unit area than muscovite. The adsorption of WEOM from a solution with 41% hydrophilic

and 59% hydrophobic components results not only from hydrophobic and hydrophilic components but also from hydrophobic and electrostatic interactions and depends on pH.

Five sample-preparation techniques to quantify 31 elements in coal HSs by ICP–AES were presented in “*Comparative Study of Sample-Preparation Techniques for Quantitative Analysis of the Mineral Composition of Humic Substances by Inductively Coupled Plasma Atomic Emission Spectroscopy*” by E. A. Karpukhina, E. A. Vlasova, D. S. Volkov, and M. A. Proskurnin [10]. It was found that the results of analysis significantly depend on the selected method of sample preparation due to specific features of HSs, the simultaneous presence of many inorganic components in wide concentration ranges, and a significant fraction of the organic matrix. Therefore, the total mineral composition of HSs, both macro- and micro-components, requires a combination of decomposition methods.

In “*The Development and Utilization of Saline–Alkali Land in Western Jilin Province Promoted the Sequestration of Organic Carbon Fractions in Soil Aggregates*” by Y. Qu, J. Tang, Z. Zhou, B. Liu, Y. Duan, J. Wang, S. Wang, Y. Li, and Z. Li [11], the effects of large macroaggregate (>2 mm, LMA), small macroaggregate (0.25 to 2 mm, SMA), and microaggregate (<0.25 mm, MA) particle size, soil layer, and soil physicochemical properties on soil organic carbon (SOC) fractions were analyzed. The results showed that the LMA size in saline-alkali paddy fields were easily decomposed and were unstable due to the influence of the external environment. With the increase in reclamation years, the proportion of LMA in the S layer decreased gradually. The readily oxidizable organic carbon, dissolved organic carbon, microbial biomass carbon, potentially mineralizable carbon, and soil organic carbon contents of aggregates in the T and S layers gradually increased with the increase in reclamation years, and SOC fractions contents of aggregates in different grain sizes were SMA > LMA > MA.

The article by E. Lodygin and E. Abakumov “*The Impact of Agricultural Use of Retisols on the Molecular Structure of Humic Substances*” [12] describes a comparison of the molecular composition of HAs and fulvic acids (FAs) extracted from virgin and arable taiga soils. The results obtained indicate that soil reclamation essentially increases the proportion of aromatic components and decreases the content of carboxyl and ester groups in the HS structure. An increased extent of hydromorphism of Retisols leads to the enrichment of HSs with aliphatic fragments.

The main task of the paper “*The Effect of Anaerobic Digestate on the Soil Organic Carbon and Humified Carbon Fractions in Different Land-Use Systems in Lithuania*” by A. Slepėtiene, M. Kochiieru, L. Jurgutis, A. Mankeviciene, A. Skersiene, and O. Belova [13] was to ascertain changes in SOC and mobile humified carbon fractions in digestate-treated soils. Authors concluded that long-term factors such as soil type and land use strongly affected the humification level (expressed as HD, %) in the soil, and the highest HD was determined in the grassland soil in Fluvisol.

In “*An Algorithm for Delimiting Rural Areas According to Soil Classes*” by J. Wójcik-Leń [14] proposes a new, self-designed algorithm for delimiting rural areas that allows the clustering of villages featuring low soil productivity, based on three factors used for determining the overall value of the area of land, share of specific type of land in the overall area of the village, and mean score for specific soil type, which allows the villages to be grouped according to classes of land occurring in the examined district. The results of the surveys provide a basis for further detailed studies into efficient management of areas featuring low soil classes during land consolidation works.

The paper “*Assessing Factors Controlling Structural Changes of Humic Acids in Soils Amended with Organic Materials to Improve Soil Functionality*” by C. Amoah-Antwi, J. Kwiatkowska Malina, E. Szara, O. Fenton, S. F. Thornton, and G. Malina [15] is devoted to understanding the effect of the OM type, frequency and duration of amendment, and pedoclimatic conditions on SOM transformation and HA structural changes. Overall, the results showed that the site (due to differences in pedoclimatic conditions), field age of OM, and amendment frequency were the main factors that influenced HA structure, and hence SOM transformation. Regular, long-term organic amendment increases the aromatic characteris-

tics of HAs, which can improve soil functionality, but short-term structural improvements are achievable only when the amending material is rich in aromatic compounds.

The study by Z. Wu, Y. Liu, G. Li, Y. Han, X. Li, and Y. Chen “*Influences of Environmental Variables and Their Interactions on Chinese Farmland Soil Organic Carbon Density and Its Dynamics*” [16] was aimed to explore the effects of natural factors, human activities, and their interactions on farmland soil organic carbon density (SOCD) and its sequestration rate (SOCDSR) by using geographical detector methods. Results of geographical detectors showed that SOCD was associated with natural factors, including groundwater depth, soil type, clay content, mean annual temperature (MAT), and mean annual precipitation. SOCDSR was related to natural factors and agricultural management, including MAT, groundwater depth, fertilization, and their interactions. Interaction effects existed in all environmental variable pairs, and the explanatory power of interaction effects was often greater than that of the sum of two single variables.

In the article by E. Shamrikova, E. Yakovleva, D. Gabov, E. Zhangurov, M. Korolev, and E. Zazovskaya titled “*Polyarenes Distribution in the Soil-Plant System of Reindeer Pastures in the Polar Urals*” [17], high-performance liquid chromatography in a gradient mode and gas chromatography-mass spectrometry methods were used to estimate the content of PAHs in mountain tundra and meadows of the Polar Urals (Russia). The results showed that the accumulation of polyarenes in soils on carbonate rocks of the Bolshoi Paipudynsky ridge occurs mainly in the process of soil formation and largely depends on factors such as productivity of plant communities, the composition of standing biomass, the site’s position in relief, the granulometric composition of soils, cryogenesis process and pyrogenesis.

The review paper “*Application of Humic Substances in Agricultural Industry*” by O. Bezuglova and A. Klimenko [18] explores the use of humic preparations as biologically active substances to increase the productivity of livestock. The authors showed that HSs formed from various natural materials are currently being tested in various branches of animal husbandry (cattle, pig breeding, poultry farming, fish farming, and fur farming), and all the information received presents convincing evidence of the high efficiency of the humates. Such materials as peat and brown coal, vegetable waste, and vermicompost can act as a source of HSs. However, in each case, more research is needed to specify the dosage and schedule of their use.

The main aim of “*The Influence of Organic and Mineral Fertilizers on the Quality of Soil Organic Matter and Glomalin Content*” by J. Balík, M. Kulhánek, J. Černý, O. Sedlář, P. Suran, and D. A. Asrade [19] is to investigate the relationship between easily extractable glomalin (EEG), total glomalin (TG), and parameters commonly used for the determination of SOM quality, i.e., the content of HAs, FAs, and potential wettability index. From the results, it is obvious that data about glomalin content can be used to study SOM quality. A more sensitive method (a method that reacts more to changes in components of soil fertility) seems to be the determination of EEG rather than TG. The factors supporting use of EEG extraction in agronomic practice are mainly the substantially shorter time of analysis than TG, HA, and FA determination and lower chemical consumption.

The article “*Distribution of Molecular Weight of Humic Substances Isolated from Soils of Tall-grass Temperate Rainforests (Chernevaya Taiga)*” by V. Polyakov, E. Abakumov, E. Lodygin, R. Vasilevich, and A. Lapidus [20] is devoted to the analysis of the molecular-weight distribution of HAs in soils of the central deciduous-forest zone of boreal forests (Chernevaya taiga, transitional ecotone forest, and coniferous forest). It has been statistically substantiated that the low-molecular-weight fraction correlates with the content of aromatic compounds and carboxyl structural fragments of HAs, which indicates the resistance of the soil organic matter of Chernevaya taiga to biodegradation.

The study by M. Yurkevich, R. Suleymanov, E. Ikkonen, E. Dorogaya, and O. Bakhmet, “*Effect of Brown Algae (*Fucus vesiculosus* L.) on Humus and Chemical Properties of Soils of Different Type and Postgermination Growth of Cucumber Seedlings*” [21] aimed to evaluate the effect of *F. vesiculosus* on the agrochemical properties of four soil types: Retisol loamy sand soil, Retisol loam, Retisol clay, and Histosol. This study showed that the effect of *F. vesiculosus*

waste application varies depending on the soil type, with the strongest impact on Retisol clay and the lowest on Histosol.

“The Molecular Composition of Humic Acids in Permafrost Peats in the European Arctic as Paleorecord of the Environmental Conditions of the Holocene” by R. Vasilevich, E. Lodygin, and E. Abakumov [22] is focused on the examination of the transformation regularities of molecular composition of HAs in the hummocky frozen peatlands of the European Arctic as a marker of climatic changes in the Holocene, and assessment of the stabilization of SOM under the conditions of modern climatic warming. Studies demonstrated that the molecules of HAs are an archive of paleoclimatic records. The Subboreal and Subatlantic climatic conditions determined the specifics of vegetation precursors and, as a result, the molecular structure of HAs in seasonally thawed layers, with a predominance of long-chain aliphatic fragments. Higher biologically active temperatures of the seasonally thawed layer of soils at bare spots (without vegetation) determined the accumulation of thermodynamically more stable HA molecules with a high content of aromatic fragments. This contributed to both the stabilization of the SOM and the conservation of peatlands in general.

In *“Chemical Characteristics of Dark-Brown Humic-like Substances Formed from the Abiotic Condensation of Maillard Precursors with Different Glycine Concentrations”* by N. Wang, Q. Zhang, W. Han, C. Bai, B. Hou, Y. Liu, and S. Wang [23], the effect of different glycine concentrations on the abiotic humification pathways and the characteristics of related products from the Maillard reaction under abiotic processes was analyzed. The results showed that (1) Under the influence of the addition of different glycine concentrations, the structure of organic molecules in the supernatant after culture tended to be simplified, and (2) The greater the concentration of glycine added, the higher proportion of aromatic C structure existed in the dark-brown residue. After culture, the structure of humic-like acids (HLA) treated by the addition of Maillard precursors became more complex, and the overall performance showed that the higher the concentration of added glycine, the more complex the HLA molecules became.

The purpose of *“Humic Acids Formation during Compositing of Plant Remnants in Presence of Calcium Carbonate and Biochar”* by N. Orlova, E. Orlova, E. Abakumov, K. Smirnova, and S. Chukov [24] is to determine the mechanism of converting the newly formed HAs into the forms with increased resistance to microbiological and biochemical influences. The understanding of HAs formation and transformation mechanisms at the early humification stages can help to optimize the methods of obtaining organic fertilizers.

The paper *“The Composition of the Organic Matter Fractions of Loamy Sand after Long-Term FYM Application without Liming”* by D. Pikuła and O. Ciotucha [25], presents the results of the effect of long-term soil fertilization with increasing doses of manure and ammonium nitrate on the composition of humus compounds not limed of loamy sand. The study showed that both crop rotation and manure fertilization significantly affected OM fractions and the humus humification index. Mineral nitrogen fertilization significantly affected the composition of the HA fraction. The large input of OM into the soil under lower content pH conditions may hinder its transformation into permanent humus.

In the article by A. Suleymanov, R. Suleymanov, V. Polyakov, E. Dorogaya, and E. Abakumov, *“Conventional Tillage Effects on the Physico-Chemical Properties and Organic Matter of Chernozems Using ^{13}C -NMR Spectroscopy”* [26], the influence of long-term conventional tillage on the water-physical, chemical properties, and composition of the OM of chernozems was examined. The results showed that the water-physical properties deteriorated in agrochernozems: the number of valuable soil aggregates decreased and the soil bulk density increased, which may limit the growth of crops. The SOM content for the different samples varied in the following direction: arable non-eroded > forest windbreak > arable eroded. It has been found that long-term plowing by conventional methods decreases aliphatic and increases aromatic structures in SOM.

The paper *“Characterization of Humic Substances from Taiga and Tundra Soils by EPR Spectroscopy”* by E. Lodygin, R. Vasilevich, and E. Abakumov [27] is devoted to the study of the influence of the degree of hydromorphism and agricultural use on the paramagnetic

properties of HA and FA samples obtained from taiga and tundra soils. Studies have shown that the increased hydromorphism in taiga soils leads to the growing concentration of free radicals (FRs) in the HA molecular structure. HAs in virgin tundra soils exhibit a lower content of unpaired electrons when shifting from automorphic soils to hydromorphic ones. The comparative analysis of the paramagnetic properties in HAs and FAs of virgin and arable soils revealed that their agricultural use reduces the FR concentration in the structure of HSs, in other words, it leads to the accumulation of biothermodynamically stable and more humified compounds in the arable horizons.

In “*Changes in the Physical, Chemical, and Bacterial Community Characteristics of Soil in Response to Short-Term Combined Organic–Inorganic Fertilizers in a Dry Direct-Seeded Paddy Field*” by X. Guo, B. Zou, L. Xu, J. Zhang, G. Zheng, H. Wang, D. Yin, H. Li, W. Zhang, Y. Lv, and M. Zhao [28], four treatments: conventional fertilization (NPK); seaweed bio-organic fertilizer + NPK; Jishiwang bio-organic fertilizer + NPK; and attapulgitic organic fertilizer + NPK applied for three consecutive years were tested to explore their effects on soil physical, chemical, and bacterial community characteristics in a dry direct-seeded rice paddy field. The correlation network analysis showed predominantly antagonistic relationships. A redundancy analysis demonstrated that total nitrogen, SOM, urease, and invertase were the main environmental factors affecting bacterial composition. Combined fertilizers may improve soil physical and chemical properties, fertility, and bacterial richness.

The study by E. Chebykina and E. Abakumov, “*Essential Role of Forest Fires in Humic Acids Structure and Composition Alteration*” [29] aimed to evaluate the molecular structure of SOM when postpyrogenic succession for results of field works in 2010 with 2020. The data obtained showed that there are significant changes in the structural organization of OM as a result of forest fires. An increase in the content of oxygen-containing groups in the HA molecules was shown for 10 years after the fires, which was accompanied by the oxidation of the HA molecule with the same increase in the aromaticity degree of the HA molecule.

“*The Coal Humic Product EldORost Shows Fertilizing and Growth Stimulating Properties on Diverse Agricultural Crops*” by O. T. Zhilkibayev, T. E. Aitbayev, A. M. Zhirkova, I. V. Perminova, A. I. Popov, S. A. Shoinbekova, M. S. Kudaibergenov, and K. M. Shalmaganbetov [30] characterized novel humic product (EldORost) from the perspective of an eco-friendly fertilizer and growth promoter. The efficiency of this novel humic product was tested in laboratory and field tests conducted on potatoes and vegetable crops (tomatoes, cucumbers, cabbage, carrots, onions, and beets). The results showed high efficiency displayed in the significantly improved sowing quality of vegetable seeds. It demonstrated that it nominally increased the germination degree and seed germination energy, intensively stimulated the side root development in plants, accelerated the growth of biomass, increased the fruiting period, and reduced maturation on the yield of potatoes and vegetable crops.

The main objective of “*Soil Organic Matter of Tidal Marsh Permafrost-Affected Soils of Kolyma Lowland*” by V. Polyakov, A. Lupachev, S. Gubin, and E. Abakumov [31] was to evaluate the SOM genesis and alteration under the influence of tidal processes in coastal permafrost-affected soils as well as to obtain the previously unknown characteristics of structural and elemental composition of different fractions of OM. The research results showed that active processes of dehydrogenation are noted in HA molecules, which indicates a relatively low degree of aliphatic structure development. According to ^{13}C NMR spectroscopy, it was revealed that up to 45% of aromatic structural fragments accumulate in HAs of marsh soils, indicating a relatively high degree of OM stabilization and resistance to biodegradation.

In all the above-mentioned articles, both the advanced scientific progress and the recently explored developments are presented. Therefore, I believe that this Special Issue will serve as a highly useful reference material for HSs and SOM researchers.

I would like to express my appreciation and heartfelt thanks to all authors, who have contributed papers to this Special Issue. Sincere thanks are also due to guest editors Prof. Evgeny Abakumov, of Saint Petersburg State University, St. Petersburg, Russia and Dr. Elena Shamrikova, of the Institute of Biology FRC Komi SC UB RAS, Syktyvkar, Russia, for

their kind help and support. The reported study was carried within the framework of the research topic of the Institute of Biology FRC Komi SC UB RAS (No. 122040600023-8).

Conflicts of Interest: The author declares no conflict of interest.

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