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Editorial

Humic Substances: Importance for Agriculture, Affinity and Interactions with Soil Amendments and Pollutants

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Humic substances (HS) represent a key component in both aquatic and terrestrial ecosystems, constituting a major pool of recalcitrant organic carbon and nitrogen. HS have a beneficiary effect on soil structure and properties, e.g., pH buffering, water retention, and cation exchange capacity. They support physiological and metabolic processes in plants, acting as promoters, biostimulants, and stress relievers. Owing to their surface functionality, HS can associate with a variety of inorganic and organic moieties (including metal ions, soil mineral phases, oxides, hydroxides, and xenobiotics) via complexation and chelation; binding of HS to immobile nutrients increases their bioavailability, while chelation with persistent hydrophobic organic contaminants and toxic metals reduces their toxicity. Therefore, humic substances regulate the dissolution and transport of nutrients, as well as the immobilization or accumulation of harmful compounds in soil horizons, facilitating pollutant sequestration. All of these features signify the essential roles HS play in sustainable agriculture and magnify the environmental benefits. The elusiveness regarding chemical and structural characterization of HS is ascribed to the variety of parent materials and genesis reactions; environmental conditions; and the diversity and intricacy of HS molecular arrangements.

This Special Issue focuses on "**Humic Substances: Importance for Agriculture, Affinity and Interactions with Soil Amendments and Pollutants**", aiming to shed light on the structural, physical, and chemical properties of HS; the characterization of HS fractions; the interactions between HS and chemical compounds related to sustainable agriculture; the influence of HS and HS-containing materials on soils, plants, and living organisms; the association of HS with toxic compounds to remove pollutants; and green methods of waste management—e.g., retention, adsorption, and composting—connected to the fate of HS.

Citation: Roulia, M. Humic Substances: Importance for Agriculture, Affinity and Interactions with Soil Amendments and Pollutants. *Agronomy* **2024**, *14*, 382. https://doi.org/10.3390/agronomy14020382

Received: 22 January 2024
Accepted: 26 January 2024
Published: 16 February 2024

In an article on the "Effect of Humic Acids on Soybean Seedling Growth under Polyethylene-Glycol-6000-Induced Drought Stress", authored by R. Matuszak-Slamani, R. Bejger, M. Włodarczyk, D. Kulpa, M. Sienkiewicz, D. Gołębiowska, E. Skórska, and A. Ukalska-Jaruga, the biostimulant properties of HS are discussed [1]. Two molecular fractions of humic acids (HA) were employed to alleviate PEG-6000-induced drought stress in soybean cultivars. The higher M_r fraction more effectively upregulated the antioxidant defense system, although no effect of either HA fraction on the macro- and micronutrient uptake was observed.

In "Calcined Oyster Shell-Humic Complex as Soil Amendment to Remediate Cd- and As-Contaminated Soil" by G. Yuan, D. Bi, J. Wei, and L. Xiao, a Ca–humic complex from leonardite-derived humic substances was prepared and employed as a soil amendment to remediate an acidic soil contaminated with Cd and As for the production of consumption-safe vegetables [2]. Pot experiments with bok choy vegetables demonstrated that the Ca–humic complex decreased the Cd and As contents in the plant by 98% and 71%, respectively, and lowered the soil Cd and As bio-accessibility in simulated gastric and intestinal compartments, reducing health risks for humans.

The "Changes in Relationships between Humic Substances and Soil Structure following Different Mineral Fertilization of *Vitis vinifera* L. in Slovakia" [3] are presented in the article authored by V. Šimanský, E. Wójcik-Gront, J. Horváthová, D. Pikuła, T. Lošák, A. Parzych, M. Lukac, and E. Aydın, aiming to reveal alterations in soil organic matter (SOM), humic substances, and soil structure, as well as their relationships under various NPK rates applied to soils with a grass sward cover. Grass cultivation in vine inter-rows considerably ameliorated the SOM, HS, and soil-structure relationships due to the addition of mineral fertilizer to the grass-covered rows.

The objective of "Deciphering the Effectiveness of Humic Substances and Biochar Modified Digestates on Soil Quality and Plant Biomass Accumulation" by J. Holatko, T. Hammerschmiedt, O. Latal, A. Kintl, A. Mustafa, T. Baltazar, O. Malicek, and M. Brtnicky is to examine the changes in labile-to-stable carbon induced by the addition of organic carbon-rich supplements to *Zea mays* L. pot experiments. Humic acid alone or combined with biochar improved the short-term nutrient (carbon, phosphorus, and nitrogen) transformation, the respiration activity, the nitrification and catabolism, the total carbon content and C/N ratio, and the long-term nitrogen mineralization [4].

Copper ions' distribution and affinity in five size-fractioned alkaline-extracted soil organic matters from paddy fields containing humic substances were investigated by W.-H. Huang, T.-C. Lin, C.-M. Huang, T.-C. Chen, and Y.-L. Yeh in their article on the "Copper Distribution and Binding Affinity of Size-Fractioned Humic Substances Taken from Paddy Soil and Correlation with Optical Characteristics" [5]. The results showed that Cu preferably associated with fractions of high aromaticity. Spectroscopic indices were significantly correlated with the ratios of metal to dissolved organic carbon.

"The Positive Effects of Humic/Fulvic Acid Fertilizers on the Quality of Lemon Fruits" were presented by X. He, H. Zhang, J. Li, F. Yang, W. Dai, C. Xiang, and M. Zhang. At different harvest times, a Eureka lemon cultivar treated with three humic/fulvic acid fertilizers produced lemons of better quality regarding the single-fruit weight, the edible rate, and the juice yield. The vitamin C, total acid, total sugar, and total soluble solid contents were higher compared with the untreated samples. The results showed that the total flavonoids and phenols in the peels, pulps, and seeds of the lemons had also increased [6].

Humic substances can alleviate soil iron deficiency in calcareous soils [7], as discussed in "Foliar Applications of Humic Substances Together with Fe/Nano Fe to Increase the Iron Content and Growth Parameters of Spinach (*Spinacia oleracea* L.)", authored by M. Turan, M. Ekinci, R. Kul, A. Kocaman, S. Argin, A.M. Zhirkova, I.V. Perminova, and E. Yildirim. Fe/nano Fe and humic/fulvic acid-based biostimulant foliar applications were performed. When combined with Fe sources, both biostimulants improved the nutrient uptake, chlorophyll contents, growth characteristics, and yield; furthermore, the biostimulants containing fulvic substances proved themselves to be even more effective at increasing the crops' yields and Fe uptake.

To promote coriander's acclimatization and tolerance against abiotic stress, "Salt-Stressed Coriander (*Coriandrum sativum* L.) Responses to Potassium Silicate, Humic Acid and Gamma Irradiation Pretreatments" were examined by R.A. Hassanein, O.S. Hussein, I.A. Farag, Y.E. Hassan, A.F. Abdelkader, and M. Ibrahim [8]. Seed priming with potassium silicate or humic acid, followed by gamma irradiation, alleviated the negative effects of salt stress and upgraded the growth parameters, yield components, and vital metabolic processes of coriander plants, including an increase in chlorophyll a/b, carbohydrates, and antioxidants and the upregulation of RuBisCO protein expression.

The "Adsorption of As(V) at Humic Acid-Kaolinite-Bacteria Interfaces: Kinetics, Thermodynamics, and Mechanisms" was investigated by M. Xiao, J. Guo, S. Zhao, and S. Li. A humic acid–kaolinite–*Bacillus subtilis* ternary composite material was prepared, which demonstrated better retention performance toward As(V) removal compared to the binary mineral–bacteria and mineral–humic acid systems [9]. Adsorption was endothermic and spontaneous and fitted the Freundlich isotherm model. The dominant mechanism behind the adsorption was the surface complexation of As(V) with the kaoline surface hydroxyl groups.

The "Impact of Care and Nutrition Methods on the Content and Uptake of Selected Mineral Elements in Solanum tuberosum" was examined by I. Mystkowska, K. Zarzecka, M. Gugała, A. Ginter, A. Sikorska, and A. Dmitrowicz. The application of five different treatments using biostimulants and herbicides in two edible potato varieties demonstrated increased P, Mg, Ca, and K uptakes compared with the control samples. The macroelement uptakes were affected by the cultivars, the herbicide–biostimulant application method, and the weather conditions [10].

Y. Escalona, D. Petrov, E. Galicia-Andrés, and C. Oostenbrink utilized IHSS HS standardized samples from various origins to create molecular systems that resemble SOM in their article entitled "Exploring the Macroscopic Properties of Humic Substances Using Modeling and Molecular Simulations" [11]. Parameters to characterize the systems' structure and dynamics including the total potential energy, density, diffusion, preferential solvation, hydrogen bonds, and salt bridges, were calculated. The number of carboxyl groups and their interactions with cations primarily determine the behavior of the studied systems, alongside, to a lesser extent, the pH, the type of cations, and the aromatic content.

Organic waste may function as an effective replacement for chemical fertilizers [12], as reported in the "Impacts of Partial Substitution of Chemical Fertilizer with Organic Manure on the Kinetic and Thermodynamic Characteristics of Soil β–Glucosidase" by R. Dong, D. Abdelkerim-Ouba, D. Liu, X. Ma, and S. Wang. Organic fertilizers increased the V_{max} of β–Glucosidase, reduced the K_m, and improved the enzyme–substrate affinity and catalytic properties of this soil enzyme, supporting the occurrence and progress of enzymatic reactions; they also effectively decreased certain thermodynamic parameters, e.g., E_a, Q_{10}, ΔH, ΔG, and ΔS.

On a similar basis, the "Effect of a Soil-Applied Humic Ameliorative Amendment on the Yield Potential of Switchgrass *Panicum virgatum* L. Cultivated under Central European Continental Climate Conditions", written by Š. Tóth and Š. Dupľák, examines four important parameters (years, nutrition, cultivars, and replications) on switchgrass yield in humic-amended soil [13]. The positive outcome of the humic ameliorative amendment to soil on the yield potential of the plant's green phytomass was verified, and nutrition was proven to be the second most influential parameter.

A simple, rapid, and reliable method for the "Quantification of Lignosulfonates and Humic Components in Mixtures by ATR FTIR Spectroscopy" [14] was developed by E.A. Karpukhina, D.S. Volkov, and M.A. Proskurnin. The proposed method can be applied in aqueous solutions and directly quantifies lignosulfonates alone or in the presence of HS. In the latter case, HS of coal origin may also be determined simultaneously. This method is practical for analyzing fertilizers of a simple composition and for the quality control of pure humates that are used to support plant growth.

A "Spectroscopic and Microscopic Analysis of Humic Acid Isolated from Stabilized Leachate HSs Fractionation" was performed by Z. Ahmed, M.S. Yusoff, N. Hana, M. Kamal, H.A. Aziz, and M. Roulia in stabilized landfill leachate of different origins. Microfiltration and centrifugation were employed to receive about 1.5 g HA/L of leachate. The isolated HA was examined via scanning electron microscopy, and by energy-dispersive X-ray, X-ray photoelectron, and Fourier transform infrared spectroscopies; UV–vis analysis revealed the significant contribution of HA to the coloration of the leachates [15].

M.A. Proskurnin, D.S. Volkov, and O.B. Rogova used specific temperature-induced changes in the band intensities, positions, and shapes of IR peaks in their article on the "Temperature Dependences of IR Spectral Bands of Humic Substances of Silicate-Based Soils" to obtain information on HS structure [16]. Attenuated total internal reflection FTIR in the mid-IR region within 298–488 K was selected to reveal the similarities and differences of HS isolated from silicate-based soils and HS originating from chernozem and soddy podzolic soils; structures formed in the dry state, skeletal vibrations were affirmed, and the behavior of polyaromatic compounds, carboxylic acids, and carboxylates was observed.

"Enhancing Soil Remediation of Copper-Contaminated Soil through Washing with a Soluble Humic Substance and Chemical Reductant" was proposed by L. Wang, J. Wei,

L. Yang, Y. Chen, M. Wang, L. Xiao, and G. Yuan as a green and sustainable method for the treatment of heavy-metal-contaminated soils. Leaching experiments performed with leonardite-derived HS coupled with $NH_2OH \cdot HCl$ demonstrated an enhanced Cu removal efficiency compared with tests using solely HS [17]. In addition, both the plant availability and bioaccessibility of Cu were reduced, while the soil pH and the organic matter content were increased.

Besides the effect of humic-amended soil on the yield of switchgrass, Š. Tóth, B. Šoltysová, Š. Dupl'ák, and P. Porvaz studied the "Impact of Soil-Applied Humic Ameliorative Amendment on the Ligno-Cellulose Quality and Calorific Value of Switchgrass *Panicum virgatum* L.". The quality parameters of acid detergent fiber, acid detergent lignin, crude cellulose, hemicellulose, neutral detergent fiber, and high heating values were evaluated. The results indicated that the cultivar, followed by the year and the nutrition, had the greatest effects on the quality factors studied [18].

A garlic–onion extract combined with a diluted bee honey solution attenuated the adverse effects of heavy-metal stress in squash plants grown in peat moss, vermiculite, crushed maize grains, and humic acid in the paper "Exploring the Role of Novel Biostimulators in Suppressing Oxidative Stress and Reinforcing the Antioxidant Defense Systems in *Cucurbita pepo* Plants Exposed to Cadmium and Lead Toxicity" by M.M. Rady, M.M.M. Salama, S. Kuşvuran, A. Kuşvuran, A.F. Ahmed, E.F. Ali, H.A. Farouk, A.S. Osman, K.A. Selim, and A.E.M. Mahmoud. These biostimulants were found [19] to interact with phytohormones, osmo-protectors, antioxidant systems, and gene expression, promoting plant growth and productivity.

The beneficial effects of HS in soil are explored in "Humate-Coated Urea as a Tool to Decrease Nitrogen Losses in Soil" [20], authored by K. Korsakov, A. Stepanov, L. Pozdnyakov, and O. Yakimenko. Urea coated with potassium humate demonstrated advantages over conventional urea by increasing the NH_4^+ nitrogen content, reducing the nitrates, and decreasing the N_2O emissions by 50%, thus lowering the nitrogen losses in the soil. Additionally, the humate-coated urea promoted both basal soil respiration and soil microbial activity, providing the highest metabolic quotient qCO_2.

"Alleviation of Water-Deficit Stress on Seed Germination of Barley and Fenugreek in a Sandy Soil Using Superabsorbent Polymer" by R.R.S. Ali, I.N. Nassar, A. Ghallab, E.F. Ali, A.I. Alqubaie, M.M. Rady, and A.A.M. Awad describes the application of a sodium polyacrylate superabsorbent polymer (SAP) mixed with air-dried sandy soil to enhance water use efficiency in water-scarce conditions [21]. Between barley and fenugreek, barley exhibited the greatest increases in the germination index and water germination efficiency after the SAP treatment.

The review article "Macromolecular Size and Architecture of Humic Substances Used in the Dyes' Adsorptive Removal from Water and Soil", authored by P.G. Fragouli, M. Roulia, and A.A. Vassiliadis, summarizes the current knowledge of the HS molecular structure and the characterization techniques employed for their study; the elusiveness regarding HS chemistry arises from their complexity and irregularity due to differences in the natural processes, in biotic and abiotic factors, in the origin of organic matter, and in the complexation of HS with inorganic species, e.g., metal ions. The adsorption of organic dyes (harmful when discharged into water or soil) on HS is discussed and mechanisms for dye-pollution management are described [22].

I would like to express my sincere thanks to all authors for their contributions; their outstanding papers summarize the latest scientific developments from different fields in this area and make this Special Issue a germane reference source for researchers focused on humic substances. In an increasingly multidisciplinary and transdisciplinary world, a dialog must be fostered amongst scientists with important contributions to upcoming research and perspectives.

The field of **Humic Substances** is gaining importance and momentum toward further innovation and progress.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

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

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