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Humic Substances: Chemistry and Multidimensional Role in Agricultural Systems and Pollution Management

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Review

Humic Substances: Bridging Ecology and Agriculture for a Greener Future

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Abstract: Humic substances (HSs) are emerging as multifunctional natural catalysts in sustainable agriculture, offering novel opportunities to enhance soil health, plant productivity, and environmental resilience. This review synthesizes recent insights into the chemical diversity, biological mechanisms, and ecological impacts of HSs, presenting a new perspective on their role as dynamic agents in agroecosystems. Derived from decomposed organic matter, HSs regulate critical processes such as nutrient cycling, carbon sequestration, and pollutant detoxification. Unlike plant and microbial biomass, which undergo rapid mineralization due to their active dynamism, HSs exhibit significant resistance to biodegradation, leading to a prolonged residence time in soil that spans years or even centuries. This stability allows HSs to maintain their functional roles over extended periods, contributing to long-term soil health and ecosystem sustainability. Their integration into agricultural systems has demonstrated profound effects, including improved soil structure, increased water retention, and the stimulation of microbial activity, which collectively bolster plant stress tolerance and yield. Notably, it has been proposed that HSs exhibit hormone-like properties, influencing plant signaling pathways to enhance root architecture and nutrient acquisition. Moreover, HSs contribute to environmental remediation by regulating the leaching of heavy metals, mitigating nutrient runoff, and fostering climate resilience. This review highlights the synergistic potential of combining HSs with organic amendments like compost and biochar, positioning HSs as a cornerstone of regenerative farming practices. Addressing challenges such as variability in composition and application methods, the discussion underscores the urgency of developing standardized approaches to harness their full potential. By framing HSs as versatile and adaptive tools, this review paves the way for advancing sustainable agricultural systems while addressing global challenges like food security and climate change.

Keywords: humic substances; sustainable agriculture; soil health; plant biostimulants; environmental resilience

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1. Introduction

1.1. Humic Substances Overview

This review synthesizes data from a broad range of peer-reviewed studies, meta-analyses, and recent advancements in soil chemistry and agricultural sciences, focusing on the role of humic substances (HSs) in soil ecosystems. The selected literature encompasses seminal works that laid the foundation for understanding the chemical and biological properties of HSs, as well as more recent studies exploring their applications in enhancing soil health and plant productivity. Comprehensive databases, including Web of Science, Scopus, and Google Scholar, were utilized to gather relevant and methodologically rigorous studies.

The body of literature spans several decades, from the foundational research of the late 20th century to contemporary contributions that address the multifaceted roles of HSs in agricultural sustainability. In total, 136 articles were analyzed, with the selection process guided by keywords such as "Humic Substances", "Humic Acids" (HAs), "Fulvic Acids" (FAs), "Humin (HU), and "Organic fertilizers from HS". This review thus offers a holistic perspective, combining historical insights with the latest developments in the field. Emphasis is placed on the influence of HSs on soil health, including their effects on soil structure, water retention, nutrient cycling, and microbial activity. Additionally, the review examines their impact on plant growth, stress resilience, and productivity (Figure 1). The potential applications of HSs in organic farming and their broader ecological implications, including carbon sequestration and biodiversity enhancement, are also discussed.

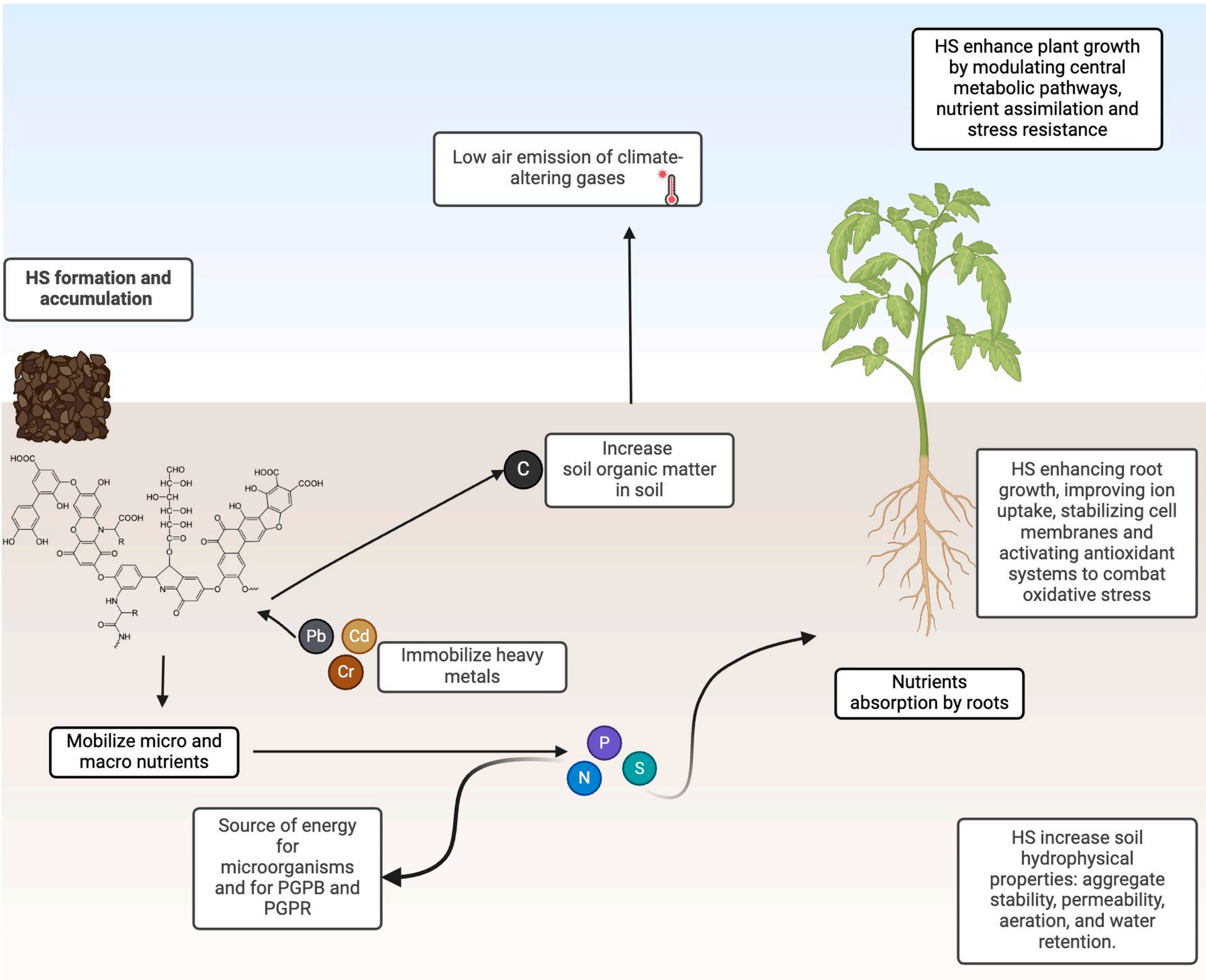

Figure 1. An overview of the role of HSs in soil, both for plants and the environment, in the context of sustainable agriculture.

Finally, the review highlights the challenges and future directions for the utilization of HSs in agricultural practices, particularly in the context of global environmental changes and the transition toward more sustainable agricultural systems.

1.2. The Role of HSs in Sustainable Agriculture

Sustainable agriculture is fundamental to addressing the growing challenges of global food security, soil degradation, and environmental sustainability in the face of climate change and population growth. By 2050, the global population is expected to reach 9.7 billion, necessitating a 70% increase in food production [1]. Unlike conventional farming, which often leads to soil erosion, water pollution, and biodiversity loss, sustainable agriculture integrates ecological principles to maintain productivity while safeguarding natural resources [2]. Core objectives include enhancing soil fertility, minimizing pollution, promoting biodiversity, and ensuring long-term economic viability for farmers [3,4]. Sustainable practices such as crop rotation, conservation tillage, organic farming, and agroforestry improve soil health and resilience [5]. Precision agriculture, which leverages digital technologies and data analytics, also supports sustainable goals by optimizing resource use and reducing environmental impact [6]. In addition, integrated nutrient management strategies, including the use of organic amendments like HSs, play a critical role in enhancing soil structure and nutrient availability [7–9]. HSs, derived from decomposed organic matter, have been identified as key contributors to sustainable soil management. They improve cation exchange capacity (CEC), water retention, and microbial diversity, which are essential for maintaining soil productivity under sustainable agricultural systems (Figure 1) [10]. Recent studies highlighted that HSs can also enhance plant resilience to drought and nutrient stress, making them particularly valuable in the context of climate change [11]. The action of HSs on plants occurs in two ways—indirectly, as a modification of soil properties, and as a direct impact on physical and metabolic plant processes. Furthermore, Nardi et al. [12] demonstrated how the HSs and their fractions positively affect primary and secondary metabolic pathways of plants both in laboratory and field studies. The considerable effect of HSs on lateral root induction and root hair growth might be caused by changes in energetic and nitrogen pathways and transport across membranes. HSs influence plant nutrition and development through closely related mechanisms that are hormone-dependent.

Adopting sustainable agricultural practices not only secures food production but also supports ecosystem services, such as pollination, pest regulation, and nutrient cycling, which are fundamental for long-term productivity [13,14]. Therefore, integrating organic matter and HSs into farming systems represents a practical strategy to enhance both soil health and agricultural sustainability [15]. Policymakers, researchers, and farmers must collaborate to implement these practices on a global scale to ensure a resilient and sustainable food system for future generations [16]. The application of HSs in agriculture has been shown to enhance plant growth, root development, and resistance to abiotic stress, making them essential for sustainable practices [17]. As a pivotal ecological force, HSs improve soil health, which is fundamental for maintaining productive and resilient agricultural systems [18].

2. Chemical and Biological Nature of HSs

2.1. Definition, Composition, and Property

HSs have been a subject of study for centuries, with their role in soil and environmental processes gradually evolving over time. Initially viewed as simple organic residues, the concept of HSs has deepened, reflecting their complex nature and ecological importance. Over the years, scientific advancements have refined their chemical classification and biological functions (Table 1). Today, HSs derived from the decomposition of plant and animal residues in the environment represent a distinct chemical class of organic compounds. According to the International HS Society (IHSS), HSs are complex, heterogeneous mixtures of polydisperse materials formed through biochemical and chemical processes during the decay and transformation of plant and microbial matter in soils, sediments, and natural waters.

Table 1. Summary of the key historical definitions of HSs, along with the associated references.

Year	Author	Definition	References
1806	Jöns Jakob Berzelius	Described HSs as dark organic matter found in Swedish water sources.	[19]
1932	Selman A. Waksman	Classified HSs into humic acid, fulvic acid, and humin, emphasizing their microbial origin.	[20]
1947	Maria V. Kononova	Defined HSs as products of organic matter decomposition, essential for soil fertility.	[21]
1972	F.J. Stevenson	Characterized HSs as heterogeneous polymers crucial for nutrient cycling and soil structure.	[22]
1989	R.S. Swift	Formalized the definitions of humic acids, fulvic acids, and humin based on solubility, via the IHSS.	[23]
2000s	IHSS 2000s	Defined HSs as heterogeneous mixtures from decomposing plant and microbial matter, important for soil health and ecosystems.	[24]

As significant components of natural organic matter (NOM), HSs are broadly classified into three fractions based on their solubility characteristics:

(1) Humic acids: soluble in alkaline conditions (range pH 8–12) become insoluble at pH 6 and precipitate in acidic environments (pH < 2);
(2) Fulvic acids: soluble in water across all pH values;
(3) Humin: insoluble in water at all pH levels [24].

The solubility characteristics reflect the traditional alkali-extraction methods of isolating these fractions from their original matrices. HSs contain chemically reactive functional groups, such as carboxyl and hydroxyl, contributing to their diverse reactivity and environmental roles. HSs' molecular weight and size vary widely, ranging from a few hundred Daltons (Da) to several hundred kilodaltons (kDa). FAs are generally of a lower molecular weight compared to HAs. The chemical composition of HSs reflects their diverse origins and the chemical processes they undergo during humification. The main components include the following:

- Carbon: Typically makes up 50–60% of the mass, present in both aromatic and aliphatic forms.
- Hydrogen: Constitutes 3–7% of the mass, primarily in aliphatic chains and as part of hydroxyl groups.
- Oxygen: Represents 30–45% of the mass, predominantly found in carboxylic, phenolic, and alcoholic groups.
- Nitrogen: Accounts for 1–5% of the mass, mainly derived from proteins, amino acids, and other nitrogenous organic materials.
- Sulfur and phosphorus: Present in minor quantities, often associated with biomolecules like lignin, nucleic acids, or microbial residues.

The elemental ratios (e.g., H/C, O/C) provide insights into the degree of aromaticity, oxidation, and humification of the material. For instance, HAs tend to have higher aromatic content than FAs, which are more oxidized and hydrophilic [24]. HSs also contain inorganic components that are integral to their structure and function in the soil. These inorganic components mainly consist of minerals, metals, and other elements that are incorporated into the humic structure through various processes such as adsorption, complexation, and co-precipitation [24].

The metal ions contained in HSs are calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^{+}), iron (Fe^{2+}, Fe^{3+}), and aluminum (Al^{3+}); these metals can bind to the functional groups in HSs, like carboxyl and phenolic groups, forming complexes that contribute to the overall structure and behavior of HSs in soils. HSs also can contain trace elements like zinc (Zn), copper (Cu), manganese (Mn), and heavy metals like lead (Pb), cadmium (Cd), and metalloids like arsenic (As) that are chelated by HSs, reducing their bioavailability in the soil and mitigating their potential [25]. Some HSs, particularly those derived from peat and lignite, may also contain small amounts of silica, which is incorporated into their structure [26].

2.2. Structural Characteristics

Although HSs lack a defined chemical structure, they are thought to consist of a matrix of aromatic rings linked by aliphatic chains and functionalized with various oxygen-containing groups. These features give HSs their charge and polarity. Carboxylic and phenolic groups confer to HS negative charges, contributing to cation exchange capacity (CEC) [27]. The interplay of polar and nonpolar groups enables interactions with water and organic pollutants [28]. Advancements in analytical techniques, such as size exclusion chromatography (SEC), have enabled the development of macromolecular structural models for HSs, providing valuable insights into the distribution of molecular sizes, the dynamic nature of HSs in various environments, and how small and heterogeneous humic molecules, with molecular masses ranging from a few hundred to a few thousand Daltons, tend to self-assemble into supramolecular conformations stabilized by weak interactions such as van der Waals forces, π–π stacking, CH–π interactions, and hydrogen bonding [28].

These assemblies contribute to the formation of micelle-like structures capable of solubilizing otherwise insoluble organic compounds, emphasizing the multifunctionality of HSs in environmental systems [29]. In aqueous environments, HSs exhibit a pronounced tendency to aggregate due to physical and chemical crosslinking. These interactions include both intra- and intermolecular forces, driven by the hydrophilic and hydrophobic functional groups attached to their aliphatic–aromatic backbones. As negatively charged entities, HSs accumulate at interfaces, where they act as mediators for organic compound solubilization and play a role in the transport of nutrients and contaminants [30]. However, due to the diversity and dynamic behavior of HSs, techniques such as size exclusion chromatography, light scattering, and viscosity measurements, which are reliable for defining polymer structures, struggle to accurately characterize these molecular assemblies.

Historically, HSs were conceptualized as large, stable macromolecular polymers within soil, often described as key structural components of soil organic matter (SOM). This view positioned HSs as significant, relatively inert molecules, playing a central role in the stabilization and long-term storage of organic carbon in soils. However, in recent years, mounting evidence has shifted the understanding of HSs from this traditional polymeric model to one of dynamic, evolving structures.

Recent studies suggest that soil organic matter should be viewed as a continuum of decomposing organic compounds rather than a fixed assembly of complex polymers. Rather than being singular, stable entities, HS are now understood as highly heterogeneous, consisting of a wide array of molecules that evolve over time through microbial decomposition and chemical processes in the soil.

Modern analytical techniques, such as advanced spectroscopic and chromatographic methods, have provided new insights into the composition and behavior of HSs. These techniques show that HSs make up only a small fraction of total organic matter (TOM), challenging the earlier assumption that they are the dominant form of organic material in soils. Instead, HSs are now viewed as "supramolecular complexes" or "super mixtures", which are collections of smaller molecules held together by non-covalent forces such as hydrogen bonding, hydrophobic interactions, and van der Waals forces. These associations, rather than persistent covalent bonds, give rise to the molecular masses and properties of humic substances. This new perspective acknowledges that HS do not possess the rigid, defined molecular structure once attributed to them. Instead, they are fluid and dynamic, with properties that change over time and in response to environmental conditions. The molecular makeup of HSs reflects the ongoing transformation of organic matter in the soil, suggesting a far more complex interaction between organic molecules, microorganisms, and soil minerals than previously thought. This alternative view emphasizes the role of HS as part of a broader system of molecular interactions, rather than as isolated, stable macromolecules.

In conclusion, the current understanding of HS reflects a significant shift in how soil organic matter is perceived. Rather than being seen as large, stable polymers, HSs are now recognized as dynamic, non-polymeric complexes whose properties are largely governed by non-covalent interactions. This shift in perspective has important implications for our understanding of soil chemistry, carbon cycling, and the roles of organic matter in soil fertility and ecosystem health (Piccolo et al., 2022; Zhao et al. 2023; Schmidt et al., 2023). Globally, HS production is estimated at approximately 10 petagrams per year, yet their precise chemical structures remain elusive [31]. The formation of HSs is highly dependent on biotic and abiotic factors, including the nature of the parent material, microbial activity, and environmental conditions. This variability underscores the challenge of unambiguously characterizing HSs while highlighting their remarkable versatility.

The unique functional properties of HSs, including their amphiphilic character, molecular size distribution, surface accessibility, and porosity, make them critical components in soil–plant systems. These properties influence the chemical and biochemical behavior of HSs, such as their role in nutrient cycling, pollutant adsorption, and soil structure enhancement. HSs are particularly effective in immobilizing heavy metals and synthetic dyes, such as azo dyes, which are persistent pollutants with harmful ecological and agricultural impacts. Addressing these challenges, HSs serve as natural agents for environmental remediation, demonstrating their importance in both terrestrial and aquatic ecosystems [32].

2.3. Sources and Formation Processes of HSs: A Modern View

The formation of HSs in soil is a complex process involving the chemical and biological transformation of organic matter derived from plant, microbial, and animal residues. The traditional formation view of HSs was based on the microbial and abiotic degradation of organic matter, followed by secondary synthesis processes. Key precursors include lignin, carbohydrates, proteins, and lipids, which undergo oxidative and enzymatic modifications. The humification process was viewed as the condensation of smaller molecules into larger, more stable macromolecules with high resilience to microbial degradation [33]. The formation of HSs occurs through two interrelated pathways. In the first, microorganisms break down complex organic materials such as lignin, cellulose, proteins, and lipids into smaller, simpler molecules such as phenols, carboxylic acids, and amino acids. In the second pathway, these reactive intermediates polymerize through condensation reactions, resulting in the synthesis of larger, more stable macromolecular structures characteristic of HSs [32]. This interconnected process transforms diverse organic inputs into HAs, FAs, and HUs, which contribute to the stability and functionality of SOC. This cycle not only highlights the pivotal role of microorganisms but also underscores the importance of abiotic factors like oxidation in forming the resilient compounds integral to soil health. The "dead-end" in the microbial degradation of SOM, which refers to stages where decomposition reaches a limit because the organic matter has become too complex or stable for microbes to further degrade, can effectively answer the critical question related to which microbes and which mechanisms can explain the catabolic and/or the anabolic processes in the case of the humus formation. Catabolic and anabolic humus process mechanisms can happen in two ways: Organic compounds, such as highly polymerized lignin or other recalcitrant materials, may reach a point where they are very difficult for microbes to break down. These compounds can become part of the humus fraction without being further degraded. The presence of such "dead-end" materials can contribute to the formation of stable humus. Microbial exhaustion: microbial activity may slow or stop when essential nutrients (like nitrogen or phosphorus) become limited or when the organic material becomes too decomposed. This can lead to a plateau in microbial degradation, where no further breakdown occurs and the SOM remains as part of the humus pool (Schmidt, et al. 2011).

A different approach, which involves initial decomposition followed by synthesis, was further refined by Kononova [34]. It posits that HSs consist of macromolecules formed de novo through the condensation of monomers. According to this theory, FAs are first produced, being of lower molecular weight, and later evolve into higher molecular weight HAs [35]. While the monomer-condensation model provides valuable insights, the degradative theories of HS formation are more widely accepted. These emphasize the oxidative degradation of biopolymers as a critical step in forming humified organic matter (HOM). This perspective is broadly endorsed by both proponents and critics of the humic concept. Supporters highlight the biodegradation of lignin, cutin, suberin, and microbial macromolecules (e.g., melanin) as significant contributors to humification. Such degradation transforms stable plant and microbial biomolecules into simpler intermediates, which are subsequently stabilized through oxidative polymerization and condensation processes. Quinone intermediates such as phenolic and lignin-derived compounds oxidize to quinones, which act as key precursors for humification. These quinones polymerize into larger, more complex structures resistant to further microbial degradation, and the chemical bonds form between different organic molecules, creating a heterogeneous mix of high-molecular-weight compounds [36]. The chemical spontaneous reactions in soils are key processes that lead to the breakdown of macromolecules into smaller units, promote the formation of stable aromatic structures, combine smaller molecules into larger, complex humic macromolecules, interact with metals to stabilize the structure of HSs and impact soil fertility by influencing nutrient availability, result in chemical bonds formed between different organic molecules, and create a heterogeneous mix of high-molecular-weight compounds. The interplay between degradation and synthesis underscores a continuum of humification, where complex macromolecular structures form from simpler precursors under specific environmental and biological conditions. This integrated perspective reconciles various theories, emphasizing the roles of both the degradation of existing biopolymers and the formation of new compounds in shaping the humic fraction of SOC.

Despite differences in the specific details proposed by various research groups regarding the polymerization and formation of HSs in soil, there is a consensus on four experimentally supported principles:

(1) Initial Degradation of Organic Matter: Dead organic matter in soil, predominantly derived from plants and soil microorganisms, undergoes partial degradation. This process breaks down complex molecules into smaller units, such as phenols, phenylpropene derivatives, amino acids, peptides, amino sugars, and simple sugars [37].
(2) Polymerization and Formation of HSs: These smaller molecules subsequently react through polymerization and polycondensation processes. These reactions are

facilitated partly by soil oxidoreductase enzymes or mineral surfaces and partly mediated by microbial activity in the soil. The resulting products are medium- to high-molecular-weight organic compounds, specifically HSs. These humic molecules further associate through supramolecular bonds, forming a dynamic network of interconnected components [38];

(3) Stability and Resistance of HSs to Degradation: these occur mainly due to the
- high stability and resistance to microbial decomposition, as many humic molecules are inherently stable against microbial enzymes;
- complexation with inorganic soil components during and after their formation, forming complexes with minerals (e.g., clay) and di- or trivalent cations like Ca^{2+}, Cu^{2+}, Fe^{3+}, and Al^{3+}. These interactions, including sorption to mineral surfaces and cation binding, significantly slow the degradation of organic matter in soil [39].

(4) Structural Models of HSs: The chemical properties and behaviors of HSs allow the development of structural models. These models commonly depict an aromatic core, though variations exist in the degree of aromaticity, molecular weight, and intramolecular bonding. Reviews by researchers such as Stevenson [22] and Schnitzer [40] provided frameworks for understanding these structures, highlighting differences in the spatial organization and chemical complexity of HSs [41].

Research revisited traditional views on humification, formation, and structure, shifting towards a model that emphasizes a continuum of decomposition reactions rather than distinct stages [42]. Despite this shift, evidence continues to support the idea that HSs are distinct molecular products formed under specific environmental conditions. Several key advancements have contributed to this nuanced understanding. Recent research has challenged traditional perspectives on humification and the nature of HSs in soil, shifting towards the "soil organic matter continuum" model [35]. This approach emphasizes a gradual transformation of organic matter rather than the creation of distinct chemical entities like HAs, FAs, and HUs. The continuum model proposes that organic matter is dynamically degraded through biological and chemical processes, forming a spectrum of decomposition products rather than specific, stable compounds, as previously thought. Critics of this model argue that distinct HSs do exist, formed through both biological and chemical reactions, including polymerization and condensation processes. These substances play essential roles in soil, such as enhancing nutrient availability, improving soil structure, and aiding microbial activity. Some researchers also highlight that humic fractions, even if operationally defined, provide valuable insights into environmental processes like nutrient cycling and contaminant binding [43]. A key debate revolves around methodological issues: traditional alkali-based extractions are criticized for potentially creating artificial results that may not represent natural soil conditions. However, proponents argue that such methods still reveal critical functional aspects of HSs in soil ecosystems. This evolving understanding has significant implications for agriculture, environmental management, and climate studies, as it refines how we conceptualize soil carbon dynamics and organic matter interactions [44]. The role of soil fauna, including organisms like insects and earthworms, facilitated humic formation through enzymatic and alkaline conditions in their digestive systems; synthesis technologies such as hydrothermal carbonization provide insights into natural processes and enable applications in soil improvement and pollution management. The integration of technologies, including hydrothermal carbonization, has enabled the synthesis of artificial HSs. These techniques, replicating natural formation processes, offer practical applications in soil improvement and pollution management. Innovation such as nuclear magnetic resonance (NMR) spectroscopy and Fourier-transform infrared (FTIR) spectroscopy have revealed detailed structural information about HSs, enhancing our understanding of their formation pathways and functional properties [45]. This nuanced view integrated traditional and modern theories, highlighting HSs as vital components of SOC with critical roles in soil fertility, nutrient cycling, and environmental health. These advancements integrate traditional theories with modern insights, underscoring HSs as essential components of SOC. They play critical roles in improving soil fertility, supporting nutrient cycling, and maintaining environmental health. The time HSs need to remain in soil to benefit soil health and plant growth can vary depending on several factors, such as soil type, climate, and the specific soil management practices in place. However, the benefits of HSs typically become noticeable over the course of several months to a few years [46–48].

Short-term benefits (months to a year): HSs begin to improve soil structure relatively quickly by promoting the aggregation of soil particles. This leads to improved soil aeration, water infiltration, and root development within a few months. They also enhance nutrient availability by increasing the CEC, allowing plants to access more nutrients.

Medium-term benefits (1 to 3 years):

As HSs continue to stabilize in the soil, their impact on soil health becomes more pronounced. Soil microbial activity increases, enhancing organic matter decomposition and nutrient cycling. The improved soil structure supports better root growth, contributing to increased plant vigor and crop yield.

Long-term benefits (3 years and beyond):

Over the long term, HSs contribute to sustained soil fertility by enhancing the soil's ability to store nutrients and water. The stabilization of organic matter helps in reducing soil erosion, improving carbon sequestration, and maintaining soil health over many years.

In summary, while HSs can start showing benefits in soil health and plant growth within months, their full impact, especially in terms of improving soil fertility and long-term plant productivity, typically takes a few years to manifest. The key is ensuring that HSs remain in the soil long enough to facilitate these lasting improvements. Additionally, the frequency of HS application is important and should be tailored to the specific needs of the soil, crop, and farming system to maximize benefits in terms of soil health, fertility, and crop productivity: For general soil health, once a year (in spring or fall). For degraded or sandy soils, twice a year or more, depending on the degradation level. For high-intensity farming or crops with high nutrient demand, two to three times a year. For organic farming or integrated soil management, annual or bi-annual application, possibly in combination with other organic amendments [47,48]. Recently, HSs have gained widespread attention as effective soil amendments due to their ability to enhance soil fertility, structure, and overall health. Notably, HSs have been shown to stabilize organic carbon in soils over the long term, offering a sustainable solution for improving soil carbon storage [49]. Furthermore, ongoing studies are focused on the integration of HSs into soil management practices, including their use in organic farming, regenerative agriculture, and greenhouse farming, where they can offer a low-cost, environmentally friendly approach to soil fertility management.

3. The Multifaceted Biological Functions of HSs

HAs serve as silent architects of life, influencing biological systems in ways that resonate far beyond their immediate presence. Emerging research reveals that these enigmatic organic compounds play a pivotal role in regulating processes at the intersection of biology and ecology, impacting everything from microbial dynamics to plant health and from nutrient cycling to ecosystem resilience. Their versatility as mediators in biochemical interactions highlights their profound influence on both individual organisms and complex ecological networks [50].

The biological functions of HSs are multifaceted and interwoven, manifesting as growth enhancement in plants, the modulation of microbial populations, and even protective effects against environmental stressors. These interactions hold transformative potential for addressing some of the most pressing environmental challenges, including soil degradation, water contamination, and the global decline in biodiversity. By mediating key processes such as nutrient availability, oxidative stress reduction, and pollutant binding, HSs emerge as critical players in promoting sustainable ecological equilibrium [51].

Knowing the dynamic interplay between HSs and biological systems and illuminating their direct and cascading effects on the environment are nowadays more and more important. Through a lens of innovation and sustainability, we explore how understanding and leveraging the unique functionalities of HSs can offer new pathways for environmental restoration, agricultural productivity, and ecosystem management. The potential of HSs to act as both mitigators of environmental stress and enhancers of biological resilience underscores their significance as a bridge between natural systems and human efforts to mitigate the pressure on the environment [52].

3.1. Soil Property Improvement

HSs positively influence soil's physical, chemical, and biological properties, thereby supporting plant growth. Although the role of HSs as growth stimulators is not a novel discovery, they have gained attention due to their effectiveness in small amounts, offering multiple benefits for plant development [52]. Among their most significant bio-stimulant effects are enhancing root systems by improving cation exchange capacity, water retention, and phosphorus availability and activating plasma membrane H^+-ATPases. They also play a role in stress tolerance [52–54]. These effects arise from interactions among SOC, microbial communities, and plant roots. These interactions contribute to improved soil structure, increased nutrient and water availability, and enhanced microbial activity, all of which help plants better withstand environmental stresses such as drought, salinity, and temperature extremes. HSs improve soil water retention and nutrient availability, reducing the negative impacts of drought stress and promoting better root development under water-limited conditions. They also stimulate the growth of beneficial soil microbes that produce growth-promoting substances, suppress pathogens, and improve the soil's resilience to biotic stresses. Moreover, HSs enhance the plant's antioxidant defense mechanisms by increasing the synthesis of stress-related compounds like phenolic acids, flavonoids, and other secondary metabolites, which help the plant manage oxidative stress induced by environmental factors. Additionally, HSs have been shown to improve soil microbial diversity, leading to a healthier soil ecosystem that supports plant growth and resilience to stress [55]. Additionally, HSs impact primary plant metabolism, enzymatic activities tied to cellular functions, and secondary metabolism. They also contribute to soil structure and aggregation, pH buffering, nutrient bioavailability, water retention, and reducing aluminum or heavy metal toxicity. However, optimizing their application to maximize crop yield and growth remains essential. Variability in HS composition, sources, and application methods creates uncertainties and diverse plant responses. Factors such as the humic source, environmental conditions, target plant species, dosage, and method of application significantly influence their effectiveness [56]. Moreover, HSs influence secondary metabolite production, aiding in stress resistance and disease mitigation [12]. They enhance enzymatic activity linked to stress responses [57] and modulate microbial communities within and beyond the rhizosphere [58]. This modulation improves processes like pathogen defense, nutrient mineralization, and solubilization [52]. Studies conducted in Egypt and in Turkey showed their role in managing plant diseases, affecting crops such as cucumber and tomato [59,60]. The authors tested three concentrations ranging from

50 to 100 and 150 ppm for each HS, HA, and FA for their efficacy in reducing pathogen growth. In vitro, FAs extracted from the green compost of plant residues and biogas manure significantly reduced pathogen growth at a concentration of 150 ppm compared to the control. FAs extracted from plant residues at concentrations of 150 ppm reduced disease severity significantly (84.7%) in relation to the other treatments. A significant increase in the total number of microorganisms in soil by HAs extracted from biogas manure with respect to other treatments have been demonstrated. All applications significantly improved the growth parameters of cucumber plants in the presence of natural inoculum, with the effects of HA treatments being more pronounced. Pathogen suppression mechanisms include microbiotas, the colonization of pathogen propagules, antibiosis, substrate competition, and induced systemic resistance [61].

3.2. Soil Functionality and Microbial Dynamics

HSs are distinguished by their complex and reactive chemical composition, which equips them to engage in a range of critical ecological processes. Their abundance of functional groups, such as carboxyl, phenolic, and quinone moieties, allows them to interact with diverse environmental components. These interactions underpin key processes including nutrient cycling, pollutant detoxification, and the stabilization of organic matter within ecosystems [62].

HSs play a pivotal role in promoting biodiversity within agricultural ecosystems by enhancing both soil microbial diversity and plant diversity. The complex molecular structure of HSs provides an abundant source of carbon and energy for beneficial soil microorganisms such as bacteria, fungi, and actinomycetes [63]. This microbial diversity is essential for nutrient cycling, disease suppression, and the overall health of the soil ecosystem [12]. Furthermore, HSs' role as signaling agents and growth promoters influences plant–microbe interactions and the establishment of symbiotic relationships, such as mycorrhizal associations, which are vital for ecosystem diversity and productivity. Recent evidence demonstrated that different molecular fractions of HSs, based on their size and composition, affect plant resilience and response mechanisms differently under stress conditions. This contributes to maintaining functional diversity in agricultural systems [64]. Recent studies showed that soils enriched with HSs exhibit increased populations of plant growth-promoting rhizobacteria and mycorrhizal fungi, which enhanced nutrient availability and plant resilience to stress [7,65]. These microbes form symbiotic relationships with plants, improving nitrogen fixation, phosphorus solubilization, and resistance to pathogens [11].

In addition to supporting microbial life, HSs improve soil structure and nutrient availability, which fosters plant diversity in agricultural systems [66]. This diversity, in turn, supports a wider range of pollinators, insects, and wildlife, enhancing ecosystem stability and resilience. The application of HSs has been shown to improve the productivity of cover crops and polyculture systems, which are critical for sustainable and regenerative agriculture [15].

Humic products (HPs) are widely applied as soil amendments to enhance plant nutrient uptake and improve agricultural productivity. However, recent research has raised questions about their broader effects on soil biology and microbial dynamics. The interaction of HPs with soil microorganisms and biochemical processes is highly complex, involving both beneficial and detrimental responses. These interactions vary depending on the type, dose, and frequency of HP application.

HPs have the ability to influence specific microbial populations, such as *Acidobacteria*, *Actinobacteria*, and *Bacteroidetes*, while also impacting enzyme activities, including laccase, peroxidase, and dehydrogenase [67]. Studies indicate that HPs can modulate microbial respiration, particularly reducing CO_2 emissions by promoting anaerobic pathways like CH_4 production under certain conditions [68]. This effect is attributed to the redox-active functional groups in HPs, which can act as electron donors and alter microbial electron flow, thus modifying both CH_4 and CO_2 emissions [69].

Moreover, HPs can have diverse effects on the soil ecosystem by influencing the microbial biomass and enzyme-mediated nutrient cycling. For instance, HPs have been implicated in influencing soil enzyme activity, which plays a central role in nutrient cycling. For instance, catalase and urease enzyme activities have been linked to improved N-cycling and overall soil fertility when HPs are applied appropriately [67].

On the other hand, the excessive application of HPs can negatively affect soil biodiversity and stability, with some studies noting reduced microbial diversity and stability at higher doses [70]. This suggests that the concentration and mode of HP application are critical for maximizing their ecological benefits while minimizing adverse effects. HSs derived from organic materials play a crucial role in stimulating microbial activity in soils, as evidenced by various studies highlighting their positive impact on soil health and fertility.

Li et al. [71] demonstrated that HSs from lignite and peat enhanced microbial diversity and activity, promoting the breakdown of organic matter and improving nutrient cycling in soil. The positive effects of HSs on soil microorganisms are attributed to their ability to serve as both a carbon source for microbes and a stimulator of microbial enzymatic activity, thereby improving soil health and nutrient availability [71]. Furthermore, Lumactud et al. [48] reported that the use of HSs led to increased microbial populations and enhanced nitrogen fixation, contributing to higher crop yields and reduced dependency on mineral fertilizers. Da Silva et al. [72] evidenced the positive effects of the inoculation of beneficial bacteria combined with the application of HSs on promoting the growth of non-leguminous plants and how this combination increased the bacterial colonization of plant hosts, showing the potential for the combined use of HSs and plant growth-promoting bacteria (PGPB) as agricultural inputs in different crops. Numerous investigations indicated that incorporating HPs into soil significantly influenced bacterial community composition and abundance, with smaller effects observed on actinomycetes, soil fungi, and microalgae populations [73–75]. Additionally, studies employing the most probable number (MPN) method revealed that HP amendments supported large populations of nitrate-reducing bacteria. In a long-term field study involving peanuts treated with HAs and inorganic fertilizers, alterations in soil enzyme activities were found to significantly impact the structure of the soil microbial community. The treatment increases the beneficial bacterial populations while reducing the abundance of harmful bacteria [76]. Additionally, the application of HAs led to an enrichment of plant-beneficial taxonomic groups, including bacterial genera within Firmicutes and fungal groups such as *Basidiomycota* and *Mortierellomycota*, which are known to enhance plant health and soil quality [77]. Variations in the physicochemical properties of HPs, experimental designs, and prevailing biotic and abiotic factors significantly influence their impact on soil microbial structure and composition. These factors determine how HPs interact with soil systems, including their ability to modulate microbial communities, enhance nutrient availability, and support plant growth.

All the multifaceted biological functions of HSs described in Section 3 are summarized in Table 2.

Table 2. Summary of multifaceted biological functions of HSs.

Key Findings	Impacts of HSs	References
Soil Property and Functionality Improvement	HSs enhance soil physical, chemical, and biological properties, improving root systems, nutrient availability, water retention, and stress tolerance. They help plants withstand environmental stresses like drought and temperature extremes.	[52–55]
Soil Microbial Activity and Disease Control	HSs stimulate beneficial soil microbes, promote growth, suppress pathogens, and improve soil resilience. They help reduce pathogen growth and disease severity in crops like cucumber and tomato. They also improve microbial diversity, nutrient cycling, and soil health.	[59–61,63]
Nutrient Cycling, Pollutant Detoxification, and Organic Matter Stabilization	HSs facilitate nutrient cycling, pollutant detoxification, and organic matter stabilization within ecosystems, supporting overall soil health.	[62]
Microbial Respiration and Enzyme Activity	HPs influence microbial respiration, reduce CO_2 emissions, and promote anaerobic processes. They also improve enzyme activity (e.g., catalase, urease), enhancing soil fertility and N-cycling.	[67–69]
Microbial Diversity, Stability, and HS Applications	Excessive HP application may reduce microbial diversity and soil stability, but optimal applications can enhance microbial community composition, including beneficial bacteria and fungi, improving plant health and soil quality. HSs, especially those derived from organic materials, stimulate microbial activity and increase microbial diversity, supporting nutrient cycling and soil fertility.	[70,71,73–77]
Combination of HSs and PGPR	HSs combined with PGPR increase bacterial colonization and crop yields and reduces the need for mineral fertilizers.	[72]

4. The Effects of HSs on Plant Growth and Physiology

4.1. Root Responses to HSs

HSs are emerging as natural growth enhancers, reshaping our understanding of plant physiology and development. By acting as bioactive catalysts, HSs influence key processes such as nutrient uptake, root architecture, and stress resilience, fostering healthier and more robust plants. Beyond conventional fertilizers, these organic compounds engage directly with cellular signaling pathways, modulate enzymatic activity, and improve soil–plant interactions, offering a sustainable and eco-friendly approach to boosting agricultural productivity [78]. Exploring the multifaceted effects of HSs on plant growth reveals a transformative tool for addressing the global challenges of food security and environmental sustainability.

The HSs emerged as vital players in the regulation of plant root growth, development, and adaptation to environmental stressors. Recent studies suggested that HSs act as signaling molecules, influencing root architecture, nutrient uptake, and stress resistance mechanisms [79]. Humic substances may also influence auxin signaling pathways. Auxin regulates gene expression by binding to receptors in plant cells, triggering a cascade of responses that control growth and development. Humic substances, through their interaction with plant root membranes and cell walls, may alter the activity of auxin receptors or affect the transport of auxins to specific target sites within the plant. By modulating these signaling pathways, humic substances can enhance or fine-tune the plant's responses to environmental stimuli, such as light, gravity, and stress. A study of Muscolo et al. [66] and Nardi et al. [12] demonstrated that HSs can induce physiological effects typical of auxin (AUX), and AUX was detected in their structure, as discussed in earlier reviews. The AUX-like effect represents one of the most well-documented phytohormonal responses triggered by HSs and has been investigated for over 50 years [56,75]. This effect is evident in morphological changes such as root elongation and the initiation of lateral root emergence, which are well-established responses to HA applications [73]. The AUX-like effects are primarily linked to the activation of the plasma membrane (PM)-bound H^+-ATPase enzymes, facilitated by small bioactive compounds with auxinic properties found in HAs, such as indole-3-acetic acid (IAA) [80]. HSs exhibit AUX-like activity, significantly influencing root growth and physiology by mimicking the action of indole-3-acetic acid (IAA), a primary AUX in plants. Research by Muscolo et al. [81] and Russel et al. [82] demonstrated that HSs modulate plant responses by stimulating plasma membrane (PM) H^+-ATPase activity, which promotes H^+ efflux and acidifies the apoplast. This results in cell wall loosening and enhanced cell expansion. Additionally, HSs influence secondary transporters, such as ZmNrt2.1 (a nitrate transporter), linked to their AUX-like effects. Further studies highlight HSs' role in signal transduction pathways mediated by enzymes like phospholipase A2 and protein kinase C, mirroring IAA's physiological responses in plants.

Data from a range of plant species indicated that specific inhibitors of AUX (2,3,5-triiodobenzoic acid and 4-chlorophenoxy-isobutyric acid) and anti-IAA antibodies can inhibit HS biological activity [83].

The interaction between auxins and HSs enhance the plant's ability to cope with environmental challenges by optimizing stress-related growth processes, such as the development of deeper root systems or the regulation of stomatal closure to conserve water, helping to regulate key developmental processes beyond root growth. HSs modulate this process by influencing auxin transport and distribution within the plant, potentially leading to more balanced shoot growth and better branching patterns. This could improve overall plant structure, supporting greater leaf area and better photosynthetic efficiency.

Numerous studies showed that the hormone-like activity is not only linked to HSs but also to composts [84] and raw materials [85]. Scaglia et al. [86] found that the dissolved organic matter from pig slurry digestate had AUX-like activity assigned to the presence of aromatic amino acids coming from the anaerobic digestion, whereas no gibberellin-like activity was detected. Later, Scaglia et al. [87] extracted substances with hormone-like activity from raw materials and corresponding vermicompost, which were well identified by using GC/MS. Carboxylic acids and amino acids were classified as molecules involved in the IAA-like activity [88].

A study evidenced that root exudates, such as phyto-siderophores, alter the structural properties and molecular conformation of HSs, creating a dynamic interaction each other's [89]. Conversely, HSs regulate the release of specific exudates, which becomes particularly relevant under conditions of stress, such as iron (Fe) deficiency [12,74]. These small molecules interact with specific cell receptors to initiate intracellular signaling pathways. This leads to the extrusion of H^+ ions via P-type ATPase enzymes, which acidifies the apoplastic space and triggers pH-sensitive enzymes. These enzymes weaken the cell wall structure, thereby promoting cell expansion by facilitating increased turgor pressure, in coordination with vacuolar-type H^+-ATPase anchored at the tonoplast membrane [90].

Moreover, the morphological effects induced by HSs closely mimic the responses triggered by IAA, as evidenced by experimental treatments with IAA inhibitors, which block root development pathways in maize treated with HAs [74].

New perspectives highlighted the role of HSs as active regulators of root phenotypic plasticity. A different study showed that HSs influenced lateral root development, root elongation, and the formation of symbiotic relationships (e.g., mycorrhizal colonization), thereby enhancing a plant's ability to access resources under varying environmental conditions, including salinity, drought, and heavy metal toxicity, by modulating oxidative stress pathways and nutrient availability [89,90]. Garnica et al. [91] explored the effects of HAs on root mechanisms in plants under iron (Fe) deficiency, with a particular focus on graminaceous species such as wheat. Their investigation was motivated by the limited scope of previous research, most of which concentrated on dicotyledonous plants and established the role of HAs in enhancing Fe solubility and bioavailability [92]. Their study specifically assessed whether a peat-extracted HA could improve Fe nutrition in both Fe-deficient and Fe-sufficient wheat. Results demonstrated that HA application improved the physiological condition of Fe-deficient plants by increasing the Fe-active pool in their leaves. This effect was likely due to the mobilization of Fe complexes via interactions between HAs and phytosiderophores released into the nutrient solution [93]. Moreover, the translocation of Fe from roots to shoots appeared to be facilitated by the phytohormone trans-Zeatin Riboside (tZR), whose concentration was notably elevated in the leaves of Fe-deficient plants treated with HAs. These findings underscored the role of HAs not only in improving Fe bioavailability, but also in enhancing hormonal signaling pathways that contribute to improved nutrient transport and plant resilience under Fe-limiting conditions [91,92]. This evolving understanding positions HSs as integral modulators of root systems rather than merely passive byproducts of organic matter decomposition. In conclusion, recent insights into root responses to HSs reveal their pivotal role in modulating root architecture and function. HSs stimulate root elongation, branching, and surface area expansion, enhancing the plant's ability to access water and nutrients. These effects are mediated through complex signaling pathways, including hormone-like activities and interactions with nutrient availability (Table 3). Such advances in understanding underscore the potential of HSs as natural agents for optimizing root development and improving plant resilience in sustainable agricultural systems.

Table 3. Summary of key studies on root responses to HSs.

Role of HSs	Key Insights	References
Auxin-like Effects on Root Growth	HSs exhibit AUX-like activity, promoting root elongation, lateral root formation, and the initiation of root development. This effect is linked to the activation of plasma membrane H^+-ATPase enzymes, which acidify the apoplast, loosen the cell wall, and enhance root cell expansion. Additionally, small bioactive compounds with auxinic properties found in HSs, such as indole-3-acetic acid (IAA), play a key role.	[12,81,82]
Modulation of Oxidative Stress and Nutrient Availability	HSs influence lateral root development, root elongation, and symbiotic relationships (e.g., mycorrhizal colonization), which improve nutrient access and plant resilience to stress, including salinity, drought, and heavy metal toxicity. These processes are often regulated through hormonal pathways and interactions with environmental stress factors.	[86,87]
Regulation of Root Exudates and Stress Response	HSs regulate root exudates under stress, particularly during Fe deficiency, by influencing the release of specific exudates. These interactions initiate intracellular signaling pathways, promoting root development and resilience under nutrient-limited conditions.	[12–92]
Hormonal Regulation in Iron Deficiency	HSs enhance Fe solubility and bioavailability, improving Fe nutrition in Fedeficient plants. This effect is associated with hormonal signaling pathways, including the translocation of Fe via phytohormones like trans-Zeatin Riboside (tZR).	[92,93]

4.2. HSs: Catalysts for Plant Physiological Adaptation

Key findings by Nardi et al. [12] underscored the role of specific functional groups within HSs in triggering both localized and systemic physiological responses in plants. These responses are mediated through intricate hormone-like signaling pathways. The biological activity of HSs is highly dependent on several factors, including their concentration, origin, molecular size, hydrophobicity, aromaticity, and the spatial arrangement of their hydrophilic and hydrophobic domains. It was brought to light that the molecular size of HSs plays a critical role in determining their mode of action [12]. Low-molecular-weight HSs can penetrate root cells and directly initiate intracellular signaling cascades, whereas high-molecular-weight HSs interact with external cell receptors to trigger downstream molecular responses. The primary targets of HSs in plants include nutrient transporters, plasma membrane H^+-ATPases, hormone signaling pathways, genes and enzymes related to nitrogen assimilation, and mechanisms governing cell division and development. Additionally, HS-induced responses extend beyond direct enzymatic activation. Genes linked to secondary nutrient transport mechanisms—such as ZmNr t2.1, a nitrate transporter—are considered key candidates for contributing to the AUX-like effects observed in plants under HA treatment [94]. Another study further demonstrated that stomatal responses, such as the opening of stomatal pores in pea epidermal tissue, were comparable to those induced by IAA treatments. This response was linked to phospholipase A2 (PLA2) and protein kinase C-like (PKC) activity, both of which are integral components of the intracellular signal transduction pathways activated by IAA in response to environmental and hormonal cues [12]. These findings highlight the multifaceted signaling mechanisms activated by HSs, mediated by both enzymatic activity and hormonal pathways. Recent work by Nardi et al. [95] evidenced that the effects of HSs were largely influenced by their molecular structure and that changes in their molecular conformation and interactions with plant roots led to diverse biological outcomes.

Pantoja-Guerra et al. [96] analyzed how the auxin-like effect in the soil–plant system modulates the plant growth-promoting activity (PGB) of *Lysinibacillus pinottii* sp. nov. PB211. The effect of HOM soil was simulated with HAs coming from vermicompost; the spectral configuration (CP/TOSS and FTIR) and coleoptile elongation test indicated its bioactivity. Cucumber exhibited a PGP effect of PB211 and HAs at a lower concentration compared to corn. This disparity agrees with the differential sensitivity to auxins of both plant models. Monocot plants, such as corn, generally exhibit greater resistance to exogenous auxin activity compared to eudicot plants, such as cucumber. The presence of HAs in the growth substrate (sand) was found to modulate the plant growth-promoting rhizobacteria (PGPR) activity of PB211, resulting in a loss of PGPR activity. Wang et al. [97], conducted a detailed study to evaluate the effects of two distinct HSs, Aojia humic acid (AHA) and Shandong humic acid (SHA), on maize (*Zea mays*) by employing foliar spraying. These HSs were previously characterized and selected based on their molecular compositions. Plant samples were collected ten days after spraying (62 days post-germination) to assess their impacts on photosynthesis, dry matter accumulation, and carbon and nitrogen metabolism, as well as broader metabolic pathways. Using Electrospray Ionization–Overpressured Layer Chromatography–Mass Spectrometry (ESI-OPLC-MS) technology, the study identified 510 small molecules with significant compositional differences between AHA and SHA. These compositional differences were reflected in the distinct biological effects on maize growth and metabolism, with AHA eliciting a more pronounced stimulatory effect compared to SHA. HSs triggered specific changes in plant metabolic pathways, enhancing carbohydrate availability, boosting energy production and metabolic flux, potentially influencing plant secondary metabolism and stress responses, and modulating nutrient and metabolite transport across cellular membranes. Rathor et al. [85] showed that the bio-stimulatory effects of HAs arise primarily from their ability to influence innate auxin and cytokinin biosynthesis pathways in plants. The authors performed analyses on the gene expression targeting pathways involved in auxin and cytokinin biosynthesis on wheat seedlings. Additionally, transgenic lines of *Arabidopsis thaliana* carrying auxin-responsive DR5 and cytokinin-responsive ARR5 promoters fused with a β-glucuronidase (GUS) reporter were employed to evaluate GUS expression in seedlings treated with HAs. The findings revealed that HA application enhanced both shoot and root growth in wheat seedlings. Genes associated with auxin biosynthesis, such as Tryptophan Aminotransferase of *Arabidopsis* and Gretchen Hagen 3.2, as well as the cytokinin biosynthesis gene Lonely

Guy3, exhibited upregulated expression in treated plants compared to controls. Furthermore, GUS expression analysis indicated that HA bioactive components triggered auxin- and cytokinin-like activities, supporting their role in modulating hormonal pathways. This research is a pioneering report utilizing ARR5:GUS transgenic lines to confirm the biostimulant properties of HAs and their potential to stimulate endogenous hormone-like responses in plants [97].

In short, the last evidence underscores that HSs influence plant development through a combination of direct and indirect mechanisms, mediated by their molecular structure, origin, and physicochemical properties. Key findings reveal that HSs enhance plant growth by modulating central metabolic pathways, nutrient assimilation, and stress resistance. For instance, they reorganize critical pathways such as starch and sucrose metabolism, the TCA cycle, and lipid biosynthesis, depending on their molecular characteristics. HSs interact with plant cell surfaces and root exudates to create dynamic molecular interactions that alter their conformation and bioactivity. This interaction enhances their efficacy in promoting root and shoot growth, increasing nutrient availability, and improving overall plant resilience. Compost-derived HAs, with higher polarity and hydrophilicity, are particularly effective, highlighting the importance of source-specific applications for maximizing benefits.

While the beneficial effects of HSs are well established, this field still requires further exploration to unravel the precise structure–function relationships and conformational dynamics driving these responses. Continued research is essential to optimize the use of HSs as sustainable tools for improving crop productivity, soil health, and stress resistance, making them indispensable in the transition to environmentally friendly agricultural practices.

4.3. HSs: Natural Stress Resilience Boosters for Plants

The HSs have garnered attention for their role in mitigating abiotic stress in plants, such as drought, salinity, heavy metal toxicity, and temperature extremes. HSs aid in stress mitigation through mechanisms like enhancing root growth, improving ion uptake, stabilizing cell membranes, and activating antioxidant systems to combat oxidative stress. Their ability to modulate hormonal balance and signaling pathways further supports plant resilience under environmental challenges, making HSs a key natural ally in sustainable agriculture [17].

Recently, Yildirim et al. [98] evidenced that HA + FA successfully mitigated the negative impacts of Cd pollution, in garden cress, by enhanced N, P, K, Ca, Mg, Fe, Mn, Cu, Mn, Zn, and B. In addition, HA + FA applications at a certain concentration successfully reduced Cd uptake by 95% and Cl uptake by 80% by decreasing H_2O_2, MDA, proline, and sucrose values. Muscolo et al. [99] isolated thirteen different HAs and FAs from diverse sources, including soils, composts, peat, leonardite, and lignite and characterized their carbon component distribution using $^{13}C^{13}C$-CPMAS NMR spectroscopy. The study utilized callus cultures of *Pinus laricio* as a model plant system to evaluate the effects of these humic extracts on growth and various biochemical parameters. These included carbohydrate and phenol content, activities of nitrogen metabolism-related enzymes (invertase, glutamine synthetase, glutamate synthase, phosphoenolpyruvate carboxylase, and malate dehydrogenase), and stress-related enzymes like catalase. The findings evidenced that humic materials enhanced callus growth, as expected, with the greatest activity exerted by the most polar HAs coming from composts. The work confirmed that HSs of various origins could act as sustainable biostimulants of plant growth and as stressor protectors by increasing phenols and antioxidant enzymes. The mechanisms underlying stress mitigation in plants encompass a diverse array of processes, including the activation of signaling pathways, induction of stress-responsive genes, accumulation of osmo-protectants and antioxidant molecules, enhancement of antioxidative metabolic activity, regulation of ion homeostasis, facilitation of membrane transport, and modulation of hormonal balance. This multifaceted response raises a compelling question: how does a complex interplay of molecules orchestrate such a wide spectrum of physiological and biochemical adaptations, enabling plants to thrive under adverse conditions? In agreement with the findings of Canellas and co-worker [17], HSs contain both pro-oxidant components, such as quinone moieties, and antioxidant groups, including phenolic hydroxyls, within their complex chemical structures [99]. This duality enables HSs to participate actively in redox reactions. The growth-promoting effects of HSs on plants may, therefore, be partly attributed to redox dynamics, influenced by the balance between pro-oxidant and antioxidant groups within their structure. Pro-oxidant moieties in HSs can contribute to reactive oxygen species (ROS) generation, triggering apoplastic oxidative bursts that play a role in signaling pathways. Conversely, antioxidant moieties, particularly polyphenolics, help regulate these oxidative bursts, preventing excessive damage. Additionally, plants respond to the oxidative environment by upregulating their intrinsic antioxidant defense systems. This coordinated interplay restores redox homeostasis, protects critical cellular components like membranes, proteins, and nucleic acids, and ultimately enhances stress tolerance, growth, and productivity. This nuanced redox-based mechanism highlights the multifaceted role of HSs in plant development and resilience.

These findings highlight the crucial role of humic substances (HSs) in promoting plant growth under optimal conditions through hormonal and metabolic effects, as well as enhancing resilience under abiotic stress by regulating redox balance and enzyme activation, summarized in Table 4.

Table 4. Summary of effect on plant growth and stress resilience of HSs.

Effect of HSs	Key Studies and Findings	References
	Optimal Conditions (Plant Growth Promotion)	
Hormonal-like effects and physiological adaptations	HSs trigger hormonal-like responses, such as auxin and cytokinin regulation, enhancing root and shoot growth. Low-molecular-weight HSs penetrate cells and initiate intracellular signals; high-molecular-weight HSs trigger cell surface receptors.	[12,88]
Molecular structure-dependent effects	Different HS sources, such as those from vermicompost, modulate plant growth-promoting bacteria (PGPB) activity in a concentration-dependent manner.	[96]
Molecular metabolism modulation	HSs impact plant metabolism, enhancing carbohydrate availability and energy production and influencing secondary metabolism and stress responses.	[97]
	Stressful Conditions (Abiotic Stress Mitigation)	
Drought, salinity, heavy metals, oxidative stress	HSs mitigate stress by enhancing root growth, ion uptake, stabilizing membranes, and activating antioxidant systems. Redox dynamics regulate oxidative bursts, balancing pro-oxidant and antioxidant activities.	[17,98,99]
Heavy metal toxicity	HSs reduce cadmium (Cd) uptake by up to 95%, Cl uptake by 80%, and protect plants from oxidative damage (reduced H_2O_2, MDA, proline, sucrose).	[98]
Redox-based stress tolerance	The antioxidant and pro-oxidant components of HSs participate in redox reactions, enhancing plant stress resilience by improving oxidative stress tolerance.	[99]
Stress-related enzyme activation	HSs increase the activity of enzymes related to nitrogen metabolism (e.g., glutamine synthetase) and stress-related enzymes (e.g., catalase).	[99]

5. Building a Greener Future: HSs in Sustainable Farming

HSs are emerging as potent biostimulants with significant implications for sustainable agriculture, owing to their multifaceted effects on plant growth and physiology. According to De Moura et al. [100], HSs demonstrated a notable ability to enhance plant metabolism when applied via foliage. The authors examined the specific traits of foliar applications and HSs across various plant categories, including vegetables, grasses, legumes, fruits, oilseeds, medicinal plants, and ornamentals. Across all plant groups, the foliar application of HSs consistently boosted parameters such as biomass production, plant height, photosynthetic pigment levels, and overall agricultural yield. Moreover, foliar-applied HSs enhanced plant resilience against stress by increasing the activity of key stress-related enzymes like peroxidase, catalase, and phenylalanine ammonium lyase (PAL). The quality of fruits treated with HSs also improved, with significant increases in sugar content, as well as higher levels of oil, protein, and fiber. For instance, research by Jan A.J et al. [101] demonstrated that the foliar application of ha improves growth and yield of chili (*Capsicum annum* L.), especially for the foliar application of HAs at the rate of 50 gL^{-1} [102]. Two recent studies on potato (*Solanum tuberosum* L.) found that the foliar application of HSs increased tuber yield [102,103]. Other researchers, on the other hand, conducted a study on the foliar application of HAs on a species of a featured in Table 1 (*Vitis Vinifera* L.) at concentrations of 5 and 20 mg L^{-1}, finding that both concentrations resulted in an increase in crop yield, berry size, chlorophyll content, N in leaves and petioles, and % TSS, as well as a reduction in fruit titratable acidity and a delay in chlorophyll degradation [104].

These improvements are attributed to the ability of HSs to enhance nutrient uptake, stimulate enzymatic activity, and improve soil health, all of which contribute to better fruit quality and nutritional content. These findings underscore the potential of HSs as an effective tool for improving the quality and marketability of fruits in agricultural systems [105]. These evidences highlighted the importance of conducting experiments across diverse plant species, environmental conditions, and sources of HSs to optimize application practices. The findings confirmed that HSs are an environmentally friendly, cost-effective technology with the potential to benefit small-scale and family farmers by improving productivity and sustainability in agriculture.

Chen et al. [106] showed that HSs play a multifaceted role in enhancing plant resilience and growth through several interconnected mechanisms. Notably, these substances aid in osmotic regulation by helping to maintain the plant's water balance and mitigating the impacts of drought stress, with important implications for sustainable agriculture due to the water savings that result from the use of HSs for crop cultivation. Ampong et al. [107] evaluated the significant impact of HAs on various aspects of crop growth and development, including plant hormone production, nutrient uptake and assimilation, yield enhancement, and protein synthesis. The effects of HAs on both soil properties and crop performance were strongly influenced by several factors, such as the type of HA, and the application identified several factors that affect HA performance in crops and soils; the most influential of them is the HA source. The HA chemical and molecular structure, solubility, and other factors such as application rate, soil, and crop type also affect HA effects on crop performance [105]. Despite the promising benefits, this review identifies critical gaps in the current understanding of HA applications. For instance, there is a lack of field studies examining the effects of HAs across diverse crop rotation systems, forms of nitrogen fertilizers, geographic locations, and varying climatic conditions. Additionally, the influence of HA and their water- and alkaline-soluble fractions, remains largely unexplored in field experiments, particularly in relation to crop yield, quality, and soil health.

Recent research highlights the benefits of integrating HSs with organic amendments for sustainable soil management. This combination has been shown to improve soil fertility, enhance nutrient availability, and foster microbial activity. For instance, studies reveal that HSs combined with organic inputs like compost or biochar significantly improve soil organic matter stability and enhance nutrient cycling, leading to better plant growth and yield [108,109]. The synergy between HSs and organic amendments facilitates the formation of stable soil aggregates, improving water retention and reducing erosion. Moreover, these mixtures enhance the bioavailability of essential nutrients like nitrogen and phosphorus while mitigating the leaching of harmful substances, contributing to environmental sustainability [110]. Advanced techniques such as two-dimensional spectroscopy (2D NMR (nuclear magnetic resonance)); 2D IR (infrared) spectroscopy; 2D UV-Vis (Ultraviolet–Visible) spectroscopy; and 2D fluorescence spectroscopy helped identify how these combinations interact with soil minerals and SOM, providing insights into mechanisms like hydrogen bonding and chelation, which improve soil structure and microbial habitats [111]. Integrating HSs with organic amendments supports a circular economy by utilizing agricultural residues and reducing dependency on mineral fertilizers. This sustainable approach aligns with modern agricultural goals, including improving productivity while reducing environmental impact [15–112]. The recent literature highlights the complementary role of biochar and HSs in improving soil health and agricultural productivity. Biochar and HSs, both rich in organic matter, can work synergistically to enhance soil properties. HSs, which are formed through the humification process of organic materials, contribute to soil aggregation, increased nutrient retention, and improved water-holding capacity. When combined, biochar and HSs can enhance soil fertility and structure more effectively than when applied alone. Biochar provides a physical framework that stabilizes HSs in the soil, reducing their leaching potential and prolonging their beneficial effects on soil properties [113].

In addition, biochar's surface has functional groups that can bind to HSs, allowing for a more stable interaction between the two materials. This binding not only increases the effectiveness of both amendments but also reduces nutrient loss and enhances microbial activity in the soil. Furthermore, biochar can increase the availability of HSs to plants by improving the soil's ability to retain these substances. Studies have shown that the combined application of biochar and HSs can lead to enhanced soil carbon sequestration, improved soil microbial health, and increased crop yields, making it a promising strategy for sustainable agriculture [114]. Wiggins et al. [115] aimed to study the effects of cantaloupe (*Cucumis melo* L.) production in organic management systems influenced by HSs and biochar. Results evidenced that HSs alone and with biochar increased the number of fruits per plant in both research trials. Fruit diameter and fruit weight in cantaloupe treated with HSs were higher compared to biochar in the 2021 research trial. Authors concluded that HSs were able to provide benefits for organic cantaloupe production inducing significant enhancements in fruit number and quality. Additionally, the combined use of HA + FA was the best treatment strategy. Ji et al. [116] tested humic-like acids, derived from municipal sludge, on rice growth, soil fertility, and dissolved organic matter, using multi-chamber root box experiments. The application of artificial HAs resulted in a notable reduction in soil electrical conductivity, indicating improved soil properties. Additionally, there was a significant increase in dissolved organic carbon content within the root zone, alongside an enhancement in the fluorescence intensity of dissolved organic matter in the rhizosphere. While the proportion of specific components of dissolved organic matter exhibited only minor changes between the rhizosphere and near-rhizosphere zones, artificial HAs were found to promote the humification process of dissolved organic matter in both the near-rhizosphere and far-rhizosphere zones. These findings highlighted the distinct environmental effects of artificial HAs compared to conventional chemical fertilizers, demonstrating their potential as a sustainable alternative. With their capacity to enhance soil organic matter dynamics and improve soil health, artificial HAs hold significant promise for advancing agricultural productivity and environmental stewardship.

The integration of HSs into agricultural practices not only boosts crop yields but also significantly enhances crop quality. By promoting the efficient adsorption of essential nutrients, these substances enrich the nutrient profile of crops and support healthier, more vigorous plant growth. Additionally, HSs play a crucial role in improving plant resilience, enabling crops to better withstand environmental stresses, which further contributes to increased productivity [117]. Beyond their direct benefits to crop production, HSs align seamlessly with the principles of sustainable agriculture. They enhance nutrient use efficiency, reducing reliance on mineral fertilizers, and thereby help lower greenhouse gas emissions and minimize nutrient run-off into aquatic ecosystems. These attributes highlight their dual role in fostering both agricultural productivity and environmental sustainability.

6. Environmental Ripple Effects of HSs

The chemical composition of HSs enables their participation in soil productivity [118]. The diverse and multifunctional nature of HSs underscores their importance in sustainable agriculture, environmental remediation, and climate change mitigation strategies.

The role of HSs in environmental remediation is multifaceted, contributing to the remediation of contaminated environments through several key mechanisms, including their ability to adsorb, stabilize, and mobilize contaminants, as well as enhance microbial activity and facilitate phytoremediation processes. Humic substances play a critical role in the adsorption of various contaminants, including heavy metals, organic pollutants, and pesticides. Through complexation and binding, HSs can stabilize these pollutants, preventing their mobility and toxicity in soil and water. For instance, HSs can bind to heavy metals, reducing their bioavailability and preventing them from leaching into groundwater [119,120]. HSs are also known to enhance the biodegradation of organic contaminants. They can improve the microbial environment by acting as carbon and energy sources for microorganisms, thus stimulating the microbial degradation of pollutants. This makes HSs an important tool in bioremediation processes, where they support the microbial breakdown of organic contaminants such as hydrocarbons [121]. Humic substances can enhance the effectiveness of phytoremediation, a process that uses plants to remove or degrade pollutants. HSs promote plant growth by improving soil structure, increasing nutrient availability, and enhancing root development. In turn, plants become more efficient in absorbing and removing contaminants from the environment [122]. In soil remediation, HSs assist in controlling pollutant bioavailability and toxicity. They can improve soil health by restoring microbial diversity and enhancing nutrient cycling, which is essential for soil recovery. HSs are particularly effective in the remediation of soils contaminated with heavy metals, hydrocarbons, and pesticides [123]. Recently, microplastic (MP) pollution, an anthropogenically driven threat to the biosphere, has emerged as a pressing global concern. A significant contributor to this issue is the accumulation of plastic residues in agricultural fields following crop cultivation. These residual plastics degrade over time into microplastics—minute particles less than 5 mm in diameter [124]. MPs profoundly affect soil's physicochemical properties, influencing porosity and enzymatic and microbial activities, and ultimately impacting plant growth and crop yield. Due to their pervasive nature, high surface area, and strong hydrophobicity, MPs act as vectors for the transport of harmful chemicals, including plasticizers, polycyclic aromatic hydrocarbons (PAHs), antibiotics, and potentially toxic elements (PTEs). Their mobility allows MPs to infiltrate deeper soil layers, posing a risk to groundwater quality. The detrimental effects of MPs on soil ecosystems include their impact on enzymatic activity, microbial diversity, plant health, and broader agricultural productivity through the spreading of toxic substances and their implications for soil and water systems. The study of microplastics (MPs) and Has remains underexplored, particularly in terms of their interactions. The findings of Klemes et al. [125] revealed that the average MP concentration in the soil surface layer (0–10 cm) was 190 $\pm$ 20 items/kg, which was significantly lower than concentrations in the 11–20 cm and 21–30 cm layers (211 $\pm$ 10 items/kg and 238 $\pm$ 18 items/kg, respectively). Additionally, larger MP particles were predominantly located in the surface layer (31.53–37.87%), whereas smaller particles were more abundant in deeper layers (73.23–100% in the 21–30 cm layer). HAs associated with MPs demonstrated a shift from low to high molecular weight with increasing depth, from 0–10 cm to 21–30 cm. This molecular change may influence the vertical distribution of MPs. These findings enhance our understanding of MP migration and underscore the need to clarify MP-HA interactions to manage MP contamination in the environment. Despite variations in HSs, optimizing their use enhances plant growth, disease control, and crop productivity.

The effectiveness of HSs in heavy metal removal has been a focal point of environmental remediation studies, with aerobic HSs (AE-HSs) emerging as particularly effective. Through advanced analytical techniques such as spectral analysis and mass spectrometry, AE-HSs have been shown to contain functional groups like phenolic compounds, carboxylic acids, and aromatic structures. These groups play a critical role in forming humates or stable complexes, which facilitate the sequestration of heavy metals from contaminated soils [126]. Optimized AE-HSs demonstrated impressive removal efficiencies of 96.18% for cadmium, 82.75% for copper, 60.43% for zinc, and 41.66% for lead, highlighting their potential in targeted heavy metal remediation [127]. These findings underscore the potential of AE-HSs derived from agricultural residues, such as straw, in developing sustainable and effective strategies for soil remediation. These studies provide new insights into the preparation and application of straw-derived HSs, emphasizing their environmental significance. Beyond heavy metal removal, HSs influence the broader ecosystem through their role in carbon sequestration, nutrient cycling, and mitigating soil degradation. Their ability to interact with pollutants and enhance microbial activity makes them valuable not only for soil remediation but also for improving soil health and sustainability in agricultural practices [128]. This underscores the importance of further research into HSs to harness their full potential for addressing environmental challenges.

6.1. HSs and Soil Carbon Stabilization

The HSs are integral to soil organic carbon (SOC) storage and long-term carbon sequestration. Their formation through the humification process results in stable organic compounds that can persist in the soil for decades or even centuries, helping to mitigate atmospheric CO_2 levels [129,130]. This sequestration process reduces greenhouse gas emissions and supports global efforts to combat climate change. According to the "humus paradigm", HSs were assumed to be complex macromolecules forming the most stable soil organic matter fraction. The stable organic matter in soils can arise from both recalcitrant (slowly degradable) and labile (easily decomposable) organic compounds and occurs as these carbon inputs interact with soil minerals and aggregates, forming stable organic complexes over time. A key question is whether both labile and recalcitrant organic matter are capable of stabilizing in soil environments, despite differences in their chemical properties and decomposition rates. This phenomenon highlights complex interactions between organic carbon inputs and soil properties, suggesting a dual mechanism for carbon stabilization driven by both biochemical recalcitrance and physical–mineral interactions [131,132].

The stability of HSs arises from their complex aromatic and aliphatic structures, which resist microbial decomposition. Practices such as adding compost, biochar, and organic amendments enhance humic substance content, improving the soil's carbon storage potential [133]. Research shows that soils rich in HSs can store up to 30% more carbon compared to degraded soils [7]. Innovative soil management strategies incorporating hydrophobic HSs are emerging as effective solutions to enhance the biological stability of soil organic matter and mitigate CO_2 emissions from agricultural soils. These management approaches capitalize on the unique properties of hydrophobic HSs, which interact with soil particles to create a more stable and resilient organic matter matrix, thereby protecting it from microbial decomposition [112]. This stabilization reduces the rate of organic matter mineralization, thereby curbing CO_2 emissions into the atmosphere.

The HSs increase microbial stability and mitigate rapid soil carbon breakdown, contributing significantly to climate change mitigation. Humic substances serving as energy sources for soil microorganisms promote their growth and metabolism. This increased microbial activity leads to more efficient organic matter decomposition, resulting in the stabilization and sequestration of carbon in the soil as stable humic compounds [134]. The microorganisms break down organic material into humus, which is more resistant to further decomposition, effectively locking carbon in the soil for longer periods.

Recent research supports their role in improving soil health by stabilizing organic matter and enhancing the overall carbon storage capacity. Furthermore, hydrophobic HSs improve soil structure by promoting the aggregation of soil particles. This aggregation enhances soil porosity and aeration, allowing for better water infiltration while reducing soil erosion risks and minimizing the release of deep carbon pools into the atmosphere [15]. The HSs reduce soil respiration rates, thereby contributing to the stabilization of organic carbon and further limiting greenhouse gas emissions [96]. The role of HSs in carbon stabilization can help to mitigate greenhouse gas emissions, aligning sustainable agriculture with global climate goals [12]. Recent experimental evidence from Spietz et al. [135] provides additional insights into the carbon sequestration potential of hydrophobic acid substances and their salts (ammonium and potassium). Their study demonstrated that HAs exhibit a CO_2 absorption capacity of up to 10.9 g CO_2 per kg, with the ammonium variant exhibiting higher CO_2 absorption rates compared to potassium salts. This suggests that HS compounds have a dual role: they not only form complex structures capable of sequestering carbon and preventing its emission, but also act as effective salts when applied to soil, enhancing the soil's ability to bind and store atmospheric CO_2. These findings highlighted the versatility of HSs, emphasizing their role as both natural carbon sinks and active soil amendments that can be used to combat climate change through innovative management practices. The combination of biological, structural, and chemical mechanisms underscores their potential for long-term climate change mitigation efforts.

6.2. HSs as Strategy to Combat Environmental Pollution

In agricultural systems, the application of HSs has been shown to reduce the leaching of nutrients such as nitrates (NO_3^-) and phosphates (PO_4^{3-}) into groundwater. HSs contain negatively charged functional groups that interact with cations, enhancing the soil's ability to retain and exchange nutrients (Table 5). This increased CEC indirectly helps to retain anions like nitrates and phosphates, reducing their movement and leaching. Additionally, HSs can form electrostatic bonds with nitrates and phosphates, especially in alkaline soils, which reduces the mobility of these nutrients and prevents leaching. This binding helps keep nutrients in the root zone for better plant uptake. By promoting soil aggregation, HSs improve soil structure, creating stable microenvironments where nutrients are less prone to leaching. This enhanced aggregation improves nutrient retention, especially during rainfall or irrigation. HSs stimulate microbial activity, which aids in nutrient cycling and the transformation of organic matter into stable forms. This process reduces nitrate leaching by converting excess nitrates into less mobile forms and enhances phosphate availability for plants. The formation of stable organic complexes between HSs and both cations and anions reduce the mobility of nutrients like nitrates and phosphates. These complexes help retain nutrients in the soil, reducing nutrient loss and improving long-term nutrient availability [136]. By enhancing nutrient retention and uptake efficiency, HSs help minimize the need for mineral fertilizers, thereby reducing chemical inputs and their associated environmental impact (Table 5). This is particularly important for addressing issues like eutrophication in freshwater bodies caused by nutrient runoff. Furthermore, organic wastes combined with HSs can further enhance this effect by creating stable organic matter complexes that trap residual agricultural pollutants, contributing to a circular economy approach in agriculture [110].

Additionally, HSs influence microbial activity by promoting beneficial microbial communities while suppressing harmful ones, further stabilizing the soil ecosystem and limiting the degradation pathways that lead to environmental pollution [137]. HSs can degrade certain organic pollutants through interactions with soil microorganisms. They facilitate the breakdown of pesticides and hydrocarbons, contributing to soil remediation and the restoration of contaminated lands [94]. This makes HSs valuable tools in bioremediation practices aimed at reducing pollution in agricultural and industrial soils (Table 5). HSs can mitigate the bioavailability and mobility of harmful contaminants, such as heavy metals and pesticides, by binding with these pollutants through complexation and chelation processes. HSs contain functional groups, such as carboxyl, hydroxyl, and phenolic groups, that can form strong complexes with heavy metals like lead (Pb), cadmium (Cd), arsenic (As), and mercury (Hg). These functional groups bind with the metals, making them less available for uptake by plants and microorganisms. HSs enhancing soil aggregation, by promoting the formation of stable aggregates, trap heavy metals within aggregate structure, reducing their mobility in the soil profile [138].

This interaction prevents these compounds from leaching into water systems and reduces their toxicity in the environment. Recent studies emphasize HSs' ability to sequester pollutants in soil matrices, enhancing the capacity of soils to retain and immobilize these compounds, thereby reducing their harmful impacts.

Innovative treatments, such as combining HSs with biochar or other organic amendments, are being explored to enhance their ability to remove contaminants from soils and water through adsorption and retention mechanisms. This highlights their versatility and potential to serve as multifunctional agents for sustainable agriculture and climate resilience [139].

The HSs have recently been recognized as having significant effects on the environmental behavior of antibiotic resistance genes (ARGs), and this area is emerging as a critical research focus [140]. The interaction of HSs with ARGs is complex, as these interactions are influenced by various environmental factors, including the presence of coexisting compounds such as antibiotics, heavy metals, and other organic particles. While the mechanisms remain partially understood, HSs have demonstrated the potential to inhibit the expression of ARGs and facilitate their removal from environmental systems, both directly and indirectly.

Research suggests that HSs interact with ARGs through various mechanisms, including electrostatic interactions, hydrophobic effects, and hydrogen bonding, all of which can alter the mobility, bioavailability, and genetic expression of ARGs in the soil–water interface. Additionally, microbial community shifts induced by the presence of HSs can impact the evolution and fate of ARGs within ecosystems. Despite these promising findings, the interaction between HSs, ARGs, and environmental co-contaminants remains underexplored, and the mechanisms of their interactions are not yet fully elucidated. Moreover, studies are sparse regarding the specific correlation between microbial populations, the environmental presence of ARGs, and HSs effects under various environmental conditions [141].

Overall, the application of HSs demonstrates promise in addressing key environmental challenges by improving soil health, reducing pollutant mobility, and fostering nutrient cycling, all while supporting sustainable agricultural practices [111].

Table 5. Role of HSs in environmental remediation technologies and their effectiveness.

Contaminant	Remediation Technology	Role of HSs	Effectiveness/Results	References
Hydrocarbons (pesticides, PAHs)	Biodegradation and Bioremediation	HSs improve the microbial environment, stimulating the biodegradation of organic contaminants through microorganisms.	Increased microbial activity that stimulates the degradation of organic contaminants like hydrocarbons and pesticides, facilitating bioremediation.	[123]
Microplastics (MP)	Adsorption and Mobilization	HSs can bind to microplastics, influencing their vertical distribution in soil and interacting with harmful chemicals.	MP-HS interactions showed a shift from low to high molecular weight with increasing depth.	[125]
Heavy Metals (Cd, Cu, Pb)	Adsorption and Stabilization	HSs bind and stabilize heavy metals, reducing their bioavailability and preventing their mobility in soil and water.	96.18% removal for cadmium, 82.75% for copper, 60.43% for zinc, 41.66% for lead (aerobic HSs).	[126,127]
Nutrients (NO_3^-, PO_4^{3-})	Leaching Prevention	HSs improve nutrient retention in soil and reduce the leaching of nitrates and phosphates.	Reduced nutrient leaching and improved plant uptake efficiency, reducing the need for synthetic fertilizers.	[136]
Heavy Metals, Pesticides	Combination with Biochar or Other Organic Amendments	HSs, combined with biochar or other organic amendments, improve adsorption and removal of contaminants from soil and water.	Greater ability to remove heavy metals and pesticides, reducing their mobility and toxicity in the environment.	[139]
Antibiotic Resistance Genes (ARGs)	Interaction with Microorganisms	HSs interact with antibiotic resistance genes (ARGs), influencing their mobility, bioavailability, and genetic expression.	Potential inhibition of ARG expression and facilitation of their removal, though studies are still limited.	[140,141]

6.3. The Economics Benefits of Using HSs in Agriculture

HSs have gained significant attention due to their potential to improve soil health, increase crop yields, and enhance nutrient efficiency. However, the profitability of using HSs in agriculture depends on several factors, including application rates, crop types, soil conditions, and regional agricultural practices. HSs improve soil structure, increase cation exchange capacity, and enhance nutrient and water retention, which results in healthier soils. This can reduce the need for mineral fertilizers, leading to cost savings in the long run. HSs also help in the immobilization of heavy metals and toxins, thus preventing soil degradation and reducing the risk of contamination, which can be costly to remediate. HSs can increase plant growth and productivity by improving nutrient availability and promoting better root development. Studies have shown that the application of HSs can lead to an increase in crop yields by 10–20%, depending on the crop type, soil conditions, and application methods [107,141]. These yield improvements translate to higher profits for farmers. One of the key advantages of using HSs is their ability to enhance nutrient retention in the soil, reducing the need for chemical fertilizers. This can be particularly beneficial in areas where fertilizer costs are high or where the environmental impact of excessive fertilizer use is a concern. By improving nutrient uptake efficiency, HSs reduce the need for frequent or high-input fertilizer applications. The application of HSs can improve carbon sequestration in soil, thus contributing to climate change mitigation efforts. Soils treated with HSs have higher organic matter content, which is important for long-term sustainability and resilience against climate change. Farmers can benefit from potential carbon credit schemes or subsidies aimed at promoting environmentally friendly farming practices [142]. The costs associated with HSs vary depending on the source (e.g., extracted from leonardite, composted organic matter, or biochar). Commercial HS products can range from USD 50 to USD 300 per ton, depending on the concentration and formulation. While this represents an upfront cost for farmers, the long-term benefits of improved soil health and productivity can offset these expenses. The recommended application rate of HSs depends on soil type, crop, and specific agricultural practices [143]. In organic or regenerative farming systems, where reducing chemical inputs is a priority, HSs offer a cost-effective alternative that aligns with sustainability goals [144]. The quality and consistency of HS products can vary, and farmers must ensure that they are purchasing high-quality, well-characterized materials that contain effective concentrations of active humic compounds. Poor-quality products may not deliver the desired benefits and could lead to financial losses [145]. One of the challenges faced by farmers in adopting HSs is the lack of awareness and knowledge about their benefits and proper application methods. Many farmers may be hesitant to adopt new practices without clear evidence of profitability [146]. Education and extension services are essential to ensure that farmers understand the value and potential of HSs. The effectiveness of HSs can vary depending on soil type, climate, and local agricultural practices. In some regions with well-developed soil management systems, the benefits of HSs may be more apparent, while in others, the costs may outweigh the benefits if the local soil conditions do not align with HS properties. The adoption of HSs is growing globally, particularly in regions with large-scale, intensive agricultural practices, such as parts of Europe, North America, and Asia. However, the economic viability is more pronounced in regions where soil degradation is a significant issue, such as in parts of Africa and Latin America, where improving soil organic matter content is critical for sustainable farming [147]. In short, while the initial costs of applying HSs may be high, their long-term benefits, such as increased crop yields, reduced fertilizer usage, and improved soil health, make them a potentially profitable investment for farmers. The economics of HSs depend on proper application rates, soil conditions, and the choice of crops. With the growing focus on sustainable agriculture and environmental protection, HSs offer an economically viable solution to improve soil fertility, enhance productivity, and reduce reliance on chemical inputs.

7. Conclusions, Challenges, and Future Directions

In conclusion, HSs, comprising HAs, FAs, and HU, hold significant promise as plant biostimulants to address the challenges of modern agriculture. These organic compounds play a pivotal role in enhancing crop productivity and sustainability by improving nutrient uptake and utilization, bolstering stress tolerance in plants, and influencing hormonal regulation. The advantages of using HSs are substantiated by various case studies across different crops, showcasing increased yields, improved crop quality, and reduced environmental impact. By facilitating nutrient absorption, promoting soil health, and enhancing stress resilience, HSs align with the goals of sustainable agriculture. However, challenges and limitations, including variations in commercial product quality, application methods, and costs, must be addressed to maximize the benefits of HSs for sustainable agricultural purposes. Rather than focusing on the traditional determination of the precise structure of HSs—a goal for which no universally accepted model has yet been achieved—the emphasis shifts toward mapping relationships and studying patterns. This approach involves moving away from purely quantitative methods toward a qualitative analysis, prioritizing the exploration of processes, environmental interactions, and plant interactions over rigid structural definitions. From this perspective, examining the balance between hydrophilic and hydrophobic components becomes crucial for understanding the environmental reactivity of HSs. This reactivity arises from the organizational processes involved in the aggregation of humic matter into macroscopic structures. Such aggregates exhibit collective behavior characterized by ordered patterns in large-scale systems while remaining less defined at the microscopic level. This macroscopic approach underscores the dynamic and emergent properties of HSs, offering valuable insights into their functional roles in environmental and biological contexts. Developing standardized guidelines for their application can help maximize their benefits, ensuring a more resilient and environmentally responsible food production system for the 21st-century growing global population.

Despite significant progress in understanding the role of HSs in biological and ecological processes, key knowledge gaps persist regarding their mechanistic functions. The complexity and heterogeneity of HS composition present challenges in identifying specific molecular interactions and pathways responsible for their effects. Limited clarity exists on how HSs influence cellular signaling, hormone-like activities, and nutrient transport at a molecular level. Additionally, variations in the bioactivity of HSs across different environmental contexts remain poorly understood. Addressing these gaps is essential for fully harnessing the potential of HSs in applications such as agriculture, environmental restoration, and biotechnology.

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