

Systematic Review

Biochar for Sustainable Agriculture: A Systematic Review and Conceptual Framework Linking Biomass Type and Pyrolysis Conditions to Soil Macronutrient Dynamics

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Abstract

Sustainable soil fertility management requires amendments that improve nutrient retention while supporting nutrient recycling. This review synthesizes current evidence on how biomass type and pyrolysis conditions determine biochar properties and, consequently, the dynamics of N, P, K, S, Ca, and Mg in soils. The analysis integrates bibliometric screening, comparative data on feedstock groups, and mechanistic evidence on adsorption–desorption, ion exchange, precipitation, microbial transformations, aging, and nutrient release. Feedstocks were grouped into agricultural, woody, animal, urban, and aquatic biomasses, whose mineral composition and structural features produced contrasting nutrient-source potentials. Across the biochars reviewed, pyrolysis temperatures ranged from 200 to 900 °C, generating materials with pH values of 4.7–13.7, surface areas of 0.18–545.66 m² g^{−1}, and nutrient contents of 0.04–8.22% N, 0.02–5.30% P, and 0.15–7.01% K. Higher pyrolysis temperatures generally increased aromaticity, alkalinity, porosity, and mineral concentration, whereas mineral-rich feedstocks provided greater direct nutrient and base-cation inputs. This review shows that BC functionality is context-dependent and should be matched to soil nutrient limitations, pH, texture, and crop requirements to improve nutrient-use efficiency and support sustainable agriculture.

Keywords: biochar; biomass type; pyrolysis conditions; soil fertility; macronutrient availability; nutrient dynamics; nutrient adsorption–desorption; nutrient retention; soil amendment; sustainable agriculture



Academic Editor: Teodor Rusu

Received: 28 May 2026

Revised: 29 June 2026

Accepted: 7 July 2026

Published: 5 August 2026

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1. Introduction

The steady increase in the global population has intensified food demand and, consequently, the pressure placed on agricultural systems. However, the intensive use of chemical fertilizers has generated adverse environmental effects, including eutrophication, greenhouse gas emissions, and soil fertility depletion, threatening long-term agricultural sustainability. In this context, the search for more sustainable alternatives has encouraged the use of residual biomass to produce organic amendments, reducing agrochemical dependence and helping close nutrient cycles within a circular economy framework.

Among the most promising alternatives are biochars (BCs), carbonaceous materials produced through the pyrolysis of biomass under controlled temperature and oxygen-limited conditions. Numerous studies have shown that BCs are effective soil amendments because of their physicochemical properties and their capacity to regulate macronutrient

dynamics [1]. These materials have a high Brunauer–Emmett–Teller (BET) specific surface area (SBET), abundant surface functional groups, and strong water- and cation-retention capacity [2–4]. Together, these properties control the adsorption, exchange, and release of essential nutrients such as nitrogen (N), phosphorus (P), sulfur (S), potassium (K), calcium (Ca), and magnesium (Mg).

The physicochemical properties of biochar (BC) depend largely on feedstock type and pyrolysis conditions, including temperature, residence time, and atmosphere. These factors influence critical parameters such as pH, electrical conductivity (EC), cation exchange capacity (CEC), porosity, and mineral composition of the material [5,6]. These properties regulate adsorption and desorption, controlling macronutrient availability and nutrient leaching in soil. For example, BCs with higher SBET and alkaline pH enhance phosphorus and ammonium retention, whereas higher CEC improves the retention of cations such as K^+ , Ca^{2+} , and Mg^{2+} [7,8].

The feedstocks used for BC production, including agricultural biomass, woody biomass, animal waste, urban waste, and aquatic biomass, contain variable proportions of minerals such as Si, P, K, Mg, Ca, and Fe. These minerals shape BC structure and determine its capacity to retain and supply nutrients [8,9]. Combined with high adsorption capacity and alkaline pH, they improve soil fertility and productivity. Consequently, BC application can optimize macronutrient availability, reduce nutrient losses through leaching, and improve fertilizer-use efficiency [10].

In addition, the porous structure and high water-retention capacity of BCs create a favorable environment for microbial activity, enhancing the biogeochemical processes that regulate nitrogen mineralization and phosphorus solubilization [11]. These combined effects make BC an effective regulator of soil fertility by simultaneously improving the physicochemical and biological functioning of soils.

Despite the growing body of research, important knowledge gaps remain regarding how feedstock type and pyrolysis conditions determine BC properties and how these properties, in turn, govern macronutrient dynamics in soil. This review provides an integrated analysis of how feedstock type and pyrolysis conditions shape the physicochemical properties of BC and how these properties regulate the availability and transformation of the macronutrients N, P, S, K, Ca, and Mg in soil.

2. Literature Search and Bibliometric Methodology

The review comprised three phases: (I) search strategy and study identification, (II) screening and eligibility assessment, and (III) bibliometric analysis and data synthesis. The review protocol was prospectively registered in the Open Science Framework (OSF; Registration ID: 5tdk9; <https://osf.io/5tdk9/>, accessed on 23 July 2026). Scopus was selected as the sole database because of its broad coverage of peer-reviewed literature in agriculture, soil science, and environmental sciences. The search strategy combined terms related to biochar, soil macronutrients, nutrient availability, biomass type, feedstock, pyrolysis, and pyrolysis temperature. To maintain the focus on agronomic nutrient management, studies primarily addressing environmental remediation or contamination were excluded, including those focused on heavy metals, organic pollutants, antibiotics, dyes, and wastewater. The search retrieved 1236 records, of which 246 duplicate records were removed before screening.

The retrieved records were screened according to predefined inclusion and exclusion criteria. Titles and abstracts were first evaluated to remove studies unrelated to biochar, soil fertility, nutrient dynamics, nutrient availability, biomass type, or pyrolysis. The remaining publications were then assessed in full to verify their relevance and consistency with the review objectives. The complete identification, duplicate removal, screening, eligibility, and inclusion process is summarized in the PRISMA flow diagram (Figure 1).

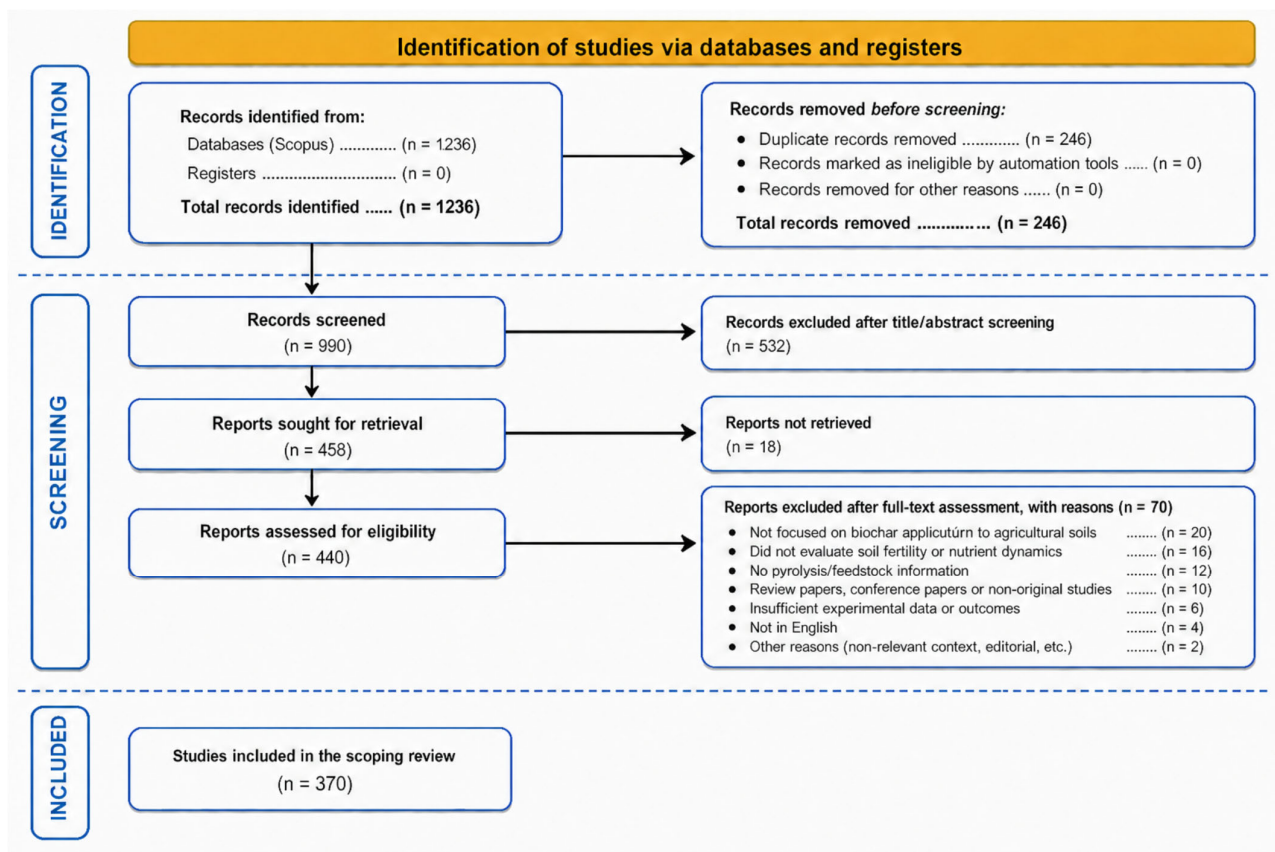


Figure 1. PRISMA flow diagram of the literature search and study selection process.

The final phase focused on bibliometric mapping and knowledge synthesis. Keyword co-occurrence analysis was performed using VOSviewer (version 1.6.20) to identify the main research themes and conceptual relationships within the selected literature (Figure 2). To improve network clarity, only representative keywords meeting the predefined occurrence threshold were retained. The resulting network identified four major thematic clusters centered on biochar, soil fertility, pyrolysis, and carbon sequestration. These clusters were associated with topics such as biomass, pyrolysis temperature, soil amendment, soil organic carbon, nutrient availability, nutrient cycling, microbial activity, crop yield, plant growth, and soil quality. The bibliometric analysis therefore complemented the systematic review by providing an overview of current research trends and the conceptual organization of the field.

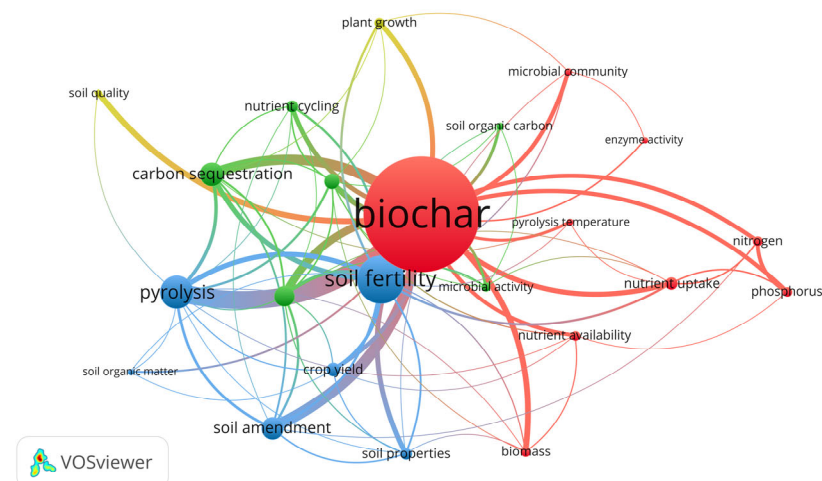


Figure 2. Keyword co-occurrence network of biochar research related to soil nutrient availability.

3. Effect of Biomass Type and Pyrolysis Conditions on the Physical and Chemical Properties of Biochar

The interaction between biomass type and pyrolysis conditions governs the physico-chemical properties of BC and, consequently, its behavior in soil. As illustrated in Figure 3, these factors collectively determine carbon content, fixed carbon, ash content, H/C and O/C atomic ratios, pH, electrical conductivity (EC), cation exchange capacity (CEC), Brunauer–Emmett–Teller (BET) specific surface area (SBET), porosity, and surface functional groups. Together, these properties regulate nutrient retention, transformation, and release, thereby controlling the availability of N, P, K, S, Ca, and Mg and ultimately influencing the agronomic performance of BC [12–14].

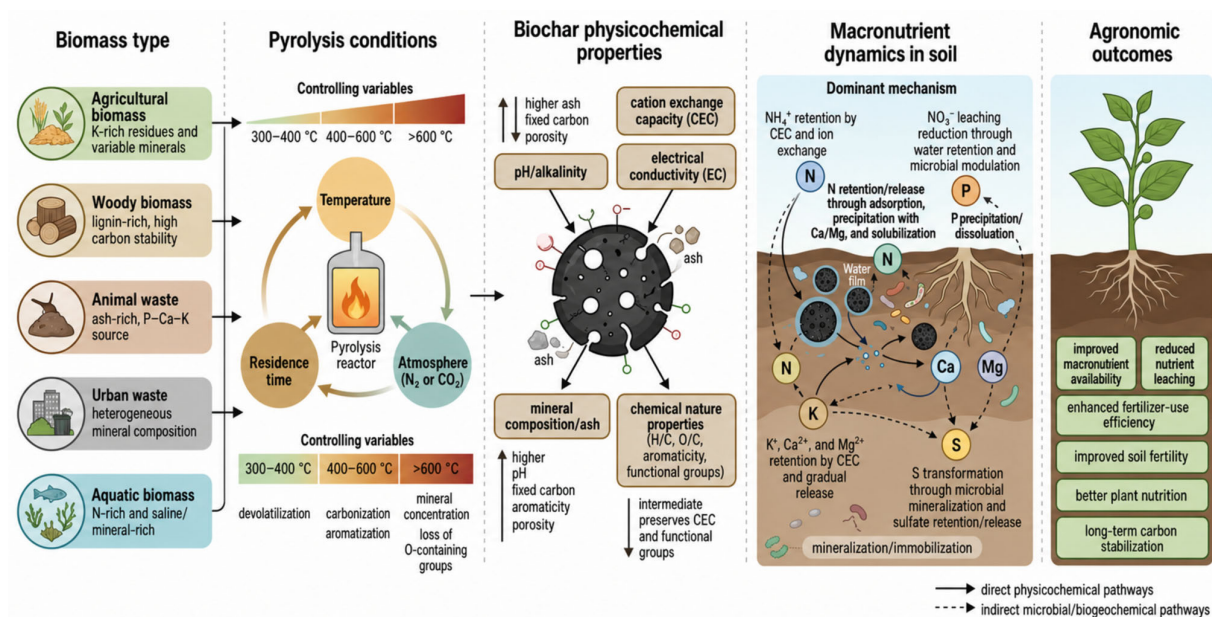


Figure 3. Integrated conceptual framework linking biomass type, pyrolysis conditions, biochar physicochemical properties, soil macronutrient dynamics, and agronomic outcomes.

From a classification perspective, the biomasses used for BC production can be grouped into five main categories: agricultural biomass, woody biomass, animal waste, urban waste, and aquatic biomass. The meta-analysis by Sun et al. [12] showed that soil response to BC application depends strongly on feedstock type, mainly through differences in pH, EC, and CEC. This variability reflects differences in lignocellulosic and mineral composition among biomass types.

Pyrolysis temperature is the main factor controlling the structural evolution of BC. During pyrolysis of lignocellulosic biomass, hemicellulose decomposes between 200 and 315 °C, cellulose between 300 and 375 °C, and lignin over a broader temperature range extending up to 900 °C [14]. These thermal transformations promote the progressive removal of volatile compounds and the relative enrichment of fixed carbon. Increasing the temperature from 400 to 500 °C significantly increases total and fixed carbon contents while reducing oxygen content and volatile matter [15]. Consequently, H/C and O/C ratios decrease, indicating greater aromaticity and structural condensation. Likewise, Qi et al. [16] evaluated BC derived from rice straw produced at 300 and 500 °C and observed differences in total carbon and nitrogen contents, confirming that pyrolysis temperature directly regulates the elemental composition of the material. These structural and compositional changes increase BC persistence in soil by enhancing aromaticity and chemical stability, thereby modifying nutrient interactions.

Increasing pyrolysis temperature also increases pH and ash content because of the relative concentration of non-volatile minerals [14]. This effect is particularly relevant for feedstocks with a higher inorganic fraction, such as agricultural biomass and animal wastes. Sun et al. [12] also showed that feedstock type significantly influences soil pH after BC application, with manure-derived BCs producing the greatest increases in soil alkalinity. This behavior is attributed to their higher mineral content.

Residence time acts synergistically with temperature. According to Wijitkosum [14], their interaction affects fixed carbon, ash content, and pH, indicating that longer exposure to elevated temperatures enhances volatile loss and the relative concentration of minerals. Nevertheless, temperature remains the predominant factor governing the final structure of BC.

Differences among biomass groups are evident even under similar pyrolysis conditions. Woody feedstocks, characterized by higher lignin content, tend to produce BCs with higher fixed carbon content and greater structural stability. In contrast, BCs derived from agricultural biomass and animal waste generally contain a higher mineral fraction, resulting in higher pH and electrical conductivity. These compositional differences are agriculturally relevant because the mineral fraction can supply nutrients and modify macronutrient availability in soil, particularly in acidic soils [17].

3.1. Pyrolysis Atmosphere as a Production Variable

Among the operational variables, pyrolysis atmosphere plays an important role in determining the physicochemical properties of BC. Whereas N₂ provides an essentially inert atmosphere, CO₂ becomes chemically active at medium and high pyrolysis temperatures, promoting gasification reactions that modify carbon structure, surface chemistry, alkalinity, porosity, and stability. These effects have been consistently reported across different feedstocks. Using walnut shells, Zhuang et al. [18] showed that CO₂ became reactive above 400 °C, promoting secondary cracking of volatile tar compounds. Consequently, aliphatic C-H groups decreased, while aromatic C=C structures increased. CO₂ also promoted partial gasification of less stable carbon structures and enhanced CO release, producing BC with an alkaline pH of 8.20. Compared with N₂, CO₂ generated a more microporous structure with greater surface reactivity.

A similar trend was reported for pine wood BC. Akgül et al. [19] found that BC produced under CO₂ had a higher pH than BC produced under N₂ (8.45 vs. 7.90). This increase results from the decomposition of acidic surface groups and the enrichment of stable mineral oxides. In addition, partial in situ gasification consumed amorphous carbon fractions that would otherwise block micropores under N₂, producing a more open pore structure. However, CO₂ also increased carbon ordering and aromaticity, reducing the thermal reactivity of BC. Although this may limit its reactivity during subsequent thermal processes, greater structural stability could enhance BC persistence in soil.

The influence of CO₂, however, depends strongly on feedstock composition. Premchand et al. [20] compared CO₂ and N₂ during slow pyrolysis at 500 °C using food waste, rice husk, and grape tree branches. Overall, BCs produced under CO₂ showed a higher average pH than those produced under N₂ (8.90 vs. 8.30), with food-waste BC reaching pH 9.71 because of carboxylic acid volatilization and the retention of mineral carbonates. Unlike the previous studies, this work also showed that CO₂ reduced solid yield and, in silica-rich rice husk, slightly decreased capacity of cation exchange compared with N₂. These findings indicate that the effects of pyrolysis atmosphere should be interpreted together with feedstock mineralogy. Overall, CO₂ pyrolysis generally produces more alkaline, aromatic, microporous, and oxidation-resistant BCs than N₂ pyrolysis. Nevertheless, its agronomic performance depends on the balance among porosity development, alkalinity,

ash retention, fixed carbon formation, surface functionality, and potential reductions in cation exchange capacity.

3.2. Surface Area and Porosity

Within the framework presented in Figure 3, surface area and porosity are the first structural properties to consider because they largely determine how BC interacts with the soil solution and regulates nutrient retention, exchange, and transformation. These properties control water and nutrient adsorption, cation exchange, and soil structural improvement, thereby influencing macronutrient availability. BC surfaces are chemically heterogeneous, containing hydrophilic and hydrophobic domains as well as acidic and basic functional sites, whose abundance depends on feedstock type and pyrolysis conditions [21]. This heterogeneity results from the incorporation of oxygen (O), nitrogen (N), phosphorus (P), and sulfur (S) into the carbon matrix, which modifies surface reactivity and affinity for different nutrient species [22,23].

Among the production variables, pyrolysis temperature exerts the greatest influence on the development of BC surface area and porosity [15,24–26]. In most lignocellulosic feedstocks, temperatures of ≥ 500 °C promote devolatilization, pore opening, and micropore formation, leading to marked increases in BET specific surface area (SBET) and pore volume [4,27–29]. For example, SBET of BC produced from apple branches increases from 2 to 109 m² g^{−1} as the pyrolysis temperature rises from 300 to 600 °C, owing to the progressive degradation of hemicellulose, cellulose, and lignin and the formation of an interconnected pore network [4,26–31]. During the early stages of pyrolysis (300–400 °C), polysaccharide decomposition initiates micropore development and generates amorphous carbon domains that enhance the retention of cations such as Ca²⁺, K⁺ and Mg²⁺ [31,32].

Further heating to 500–600 °C intensifies lignin decomposition and the release of gaseous products (H₂ and CH₄), expanding the microporous structure [8,33,34]. However, this trend is not universal and depends strongly on feedstock composition. In silica-rich biomasses, such as rice husks and rice straw, high ash contents promote micropore blockage at temperatures ≥ 800 °C, reducing SBET and limiting nutrient access to adsorption sites [35]. By contrast, lignin-rich woody biomasses continue developing a more stable and highly porous carbon matrix, favoring nutrient adsorption and long-term persistence in soil [36]. These contrasting responses demonstrate that the effect of increasing temperature is governed not only by thermal severity but also by the mineralogical composition of the feedstock.

Beyond modifying BC structure, these properties also influence soil physical quality. BC application increases soil porosity by 2–41% [37] and improves aeration, aggregate formation, thereby enhancing water retention and root development [38,39]. These improvements are generally more pronounced in coarse-textured soils because BC increases pore-size diversity and creates a more favorable habitat for microbial activity. Consequently, surface area and porosity connect BC structural characteristics with its agronomic performance by regulating nutrient retention and availability in soil.

The comparative data summarized in Table 1 further illustrate these relationships. Agricultural and woody biomasses consistently produce the highest SBET values because their lignocellulosic structure favors micropore development during pyrolysis. As temperature increases to approximately 600–800 °C, coconut shell reaches 514.3 m² g^{−1} at 700 °C [40], palm kernel shell 403.99 m² g^{−1} at 650 °C [41], Douglas fir wood 490 m² g^{−1} at 600 °C [42], and pruning wood chips from apple trees 545.66 m² g^{−1} at 800 °C [43]. These increases are accompanied by greater pore volume, as illustrated by palm kernel shell (0.330 cm³ g^{−1} at 650 °C [41]), confirming that devolatilization and aromatic carbon rearrangement promote the formation and stabilization of micropores. Within this biomass

group, dense lignin-rich feedstocks generally achieve the largest surface areas, whereas silica-rich or less compact materials show more moderate pore development.

In contrast, Table 1 shows that BCs produced from animal and urban wastes generally develop much lower SBET values, even at comparable temperatures. Sewage sludge reaches $67.3 \text{ m}^2 \text{ g}^{-1}$ at 600°C [44], whereas most livestock residues remain below $50 \text{ m}^2 \text{ g}^{-1}$, except for bovine manure, which reaches $186.5 \text{ m}^2 \text{ g}^{-1}$ at 600°C [25]. This difference reflects the higher mineral and ash contents of these feedstocks, which restrict micropore formation and promote sintering during pyrolysis. Therefore, increasing pyrolysis temperature does not produce the same structural response across all biomass types. Lignocellulosic feedstocks primarily enhance nutrient retention through greater surface area and pore development, whereas mineral-rich feedstocks rely more on their chemical composition than on structural properties. Overall, these findings indicate that both feedstock composition and pyrolysis temperature must be considered together when selecting BCs for improving macronutrient retention, soil fertility, and fertilizer-use efficiency.

Table 1. Summary of the physicochemical characteristics of BCs derived from different biomass categories, condensed from the original Table S1 (Supplementary Material).

Biomass Category	Typical T_{pyr} * Range ($^\circ\text{C}$)	Main Physicochemical Characteristics	Dominant Properties	Implications for Macronutrient Dynamics	Reference
Agricultural biomass	250–800	pH: 4.7–11.3; EC: $0.08\text{--}38.0 \text{ dS m}^{-1}$; SBET: $0.18\text{--}514.3 \text{ m}^2 \text{ g}^{-1}$; CEC: $0.5\text{--}649.0 \text{ cmol}^+ \text{ kg}^{-1}$	Highly variable mineral composition and surface functionality	Can simultaneously supply nutrients and enhance nutrient retention, particularly for K, Ca and Mg, depending on feedstock and pyrolysis severity.	[40,45–47]
Woody biomass	300–800	pH: 5.1–11.1; EC: $0.01\text{--}7.1 \text{ dS m}^{-1}$; SBET: $0.71\text{--}545.7 \text{ m}^2 \text{ g}^{-1}$; CEC: $0.8\text{--}65.0 \text{ cmol}^+ \text{ kg}^{-1}$	Greater aromaticity, carbon stability and pore development.	Primarily improves nutrient retention, water-holding capacity and long-term soil carbon storage.	[3,4,14,35,48]
Animal waste	200–750	pH: 7.2–12.6; EC: $0.19\text{--}23.8 \text{ dS m}^{-1}$; SBET: $0.92\text{--}186.5 \text{ m}^2 \text{ g}^{-1}$; CEC: $5.9\text{--}75.3 \text{ cmol}^+ \text{ kg}^{-1}$	High ash content and abundant nutrient-bearing minerals.	Strong nutrient-source potential and high capacity to retain NH_4^+ and phosphate through mineral interactions.	[25,48–51]
Urban waste	300–900	pH: 6.4–11.8; EC: $0.22\text{--}7.6 \text{ dS m}^{-1}$; SBET: $3.5\text{--}67.3 \text{ m}^2 \text{ g}^{-1}$; CEC: $2.9\text{--}29.0 \text{ cmol}^+ \text{ kg}^{-1}$	Heterogeneous composition and moderate mineral content.	May improve nutrient retention and recycling of urban residues, although feedstock quality must be carefully controlled.	[46,50,52–54]
Aquatic biomass	200–800	pH: 8.7–13.7; EC: $12.4\text{--}30.3 \text{ dS m}^{-1}$; SBET: $6.5\text{--}134.2 \text{ m}^2 \text{ g}^{-1}$; CEC: $49.8\text{--}81.2 \text{ cmol}^+ \text{ kg}^{-1}$	Highly alkaline and mineral-rich BCs.	High nutrient contribution and cation exchange capacity, but with greater salinity risk under repeated application.	[55,56]

* Pyrolysis temperature (T_{pyr}).

3.3. pH

Among the physicochemical properties of BC, pH is one of the main factors controlling soil acidity, nutrient availability, and microbial activity. It is primarily governed by feedstock composition and pyrolysis temperature, although the degree of oxidation also contributes to its final value [57,58]. In general, increasing pyrolysis temperature raises BC pH because thermal decomposition concentrates inorganic minerals in the ash fraction while progressively removing acidic surface groups [59,60].

Above approximately 350 °C, carbonates, oxides, and hydroxides of Ca, Mg, K, and Na become progressively enriched as the organic matrix decomposes, increasing the abundance of basic cations and reducing surface acidity [25]. Consequently, BCs produced at 300–400 °C generally exhibit neutral to slightly alkaline pH (7–8), whereas materials produced at ≥ 600 °C commonly reach pH values between 9 and 12 [60]. This alkalization results from the combined effects of ash enrichment, the loss of acidic functional groups (-COOH and -OH), and the deprotonation of oxygen-containing surface functionalities [31].

Ash content is closely associated with this trend. Enders et al. [61] reported that BCs containing less than 8% ash had pH values below 8.6, whereas those with more than 30% ash exceeded pH 10. Likewise, Yuan et al. [62] observed that increasing pyrolysis temperature from 300 to 500 °C raised BC pH from 7.5 to 11.6, which was attributed to the accumulation of alkaline minerals, including CaCO_3 , MgCO_3 , K_2O . Similarly, BCs combining low H/C ratios with high ash contents consistently exhibit the highest pH values [5].

Feedstock composition further explains the variability reported among BCs produced under similar thermal conditions. Mineral-rich feedstocks, including manures, food waste, and seed husks, generally produce more alkaline BCs than woody lignocellulosic materials. For example, BCs derived from chicken manure, soybean husks, and paper waste reached pH values of 11.8, 11.3, and 11.1, respectively [63]. In contrast, lignocellulosic feedstocks exhibit a more gradual increase in pH with temperature. Jindo et al. [35] reported that rice husk BC increased from pH 6.8 to 9.6, whereas Komnitsas et al. [64] observed an increase from 4.7 to 8.8 for pistachio shell BC as pyrolysis temperature increased from 400 to 800 °C.

These differences have important agronomic implications because BC pH directly influences macronutrient behavior in soil. Moderately alkaline BCs (pH 8–10) improve phosphate availability, enhance the retention of Ca^{2+} , Mg^{2+} and K^+ , and reduce aluminum and manganese toxicity in acidic soils [65,66]. However, excessively alkaline BCs (pH > 11) may promote the precipitation of calcium and magnesium phosphates while decreasing the availability of micronutrients such as Fe, Mn, and Zn [67]. Therefore, the optimal BC pH depends on soil conditions and should provide sufficient acidity correction without compromising nutrient availability.

The comparative data in Table S1 confirm that both feedstock type and pyrolysis temperature determine the final pH of BC. Agricultural and woody feedstocks generally evolve from acidic or near-neutral values at low temperatures to strongly alkaline values as pyrolysis severity increases. For example, pistachio shell increased from pH 4.7 at 300 °C [64], palm kernel shell from 5.5 at 300 °C [68], and disposable bamboo chopsticks from 6.7 at 400 °C [14], whereas corn stover, sawdust, and woody green waste reached pH values above 10 between 600 and 800 °C [46,50,69]. These changes reflect progressive ash concentration and the continuous removal of oxygen-containing acidic functional groups during carbonization. Feedstocks with higher initial mineral contents consistently reached higher pH values, whereas those containing fewer inorganic constituents exhibited a more moderate increase. Residence time had a secondary effect, slightly enhancing alkalinity by promoting more complete carbonization.

In contrast, Table S1 shows that BCs produced from animal and urban wastes remain highly alkaline even at relatively low pyrolysis temperatures because their mineral-rich composition dominates their chemical behavior. Animal-derived BCs typically exhibit pH values between 7.2 and 12.6 [51], whereas algal biomass reached pH 13.7 at 600 °C [70]. Unlike lignocellulosic feedstocks, increasing temperature mainly reinforces an already alkaline material rather than causing a pronounced pH shift. This comparison highlights two distinct pathways of alkalinity development: thermal-induced alkalization in lignocellulosic feedstocks and intrinsically high alkalinity in mineral-rich feedstocks.

Consequently, selecting BC for agricultural use should consider not only its final pH but also the origin of that alkalinity, as this influences nutrient retention mechanisms and its capacity to improve soil fertility.

3.4. Electrical Conductivity

Electrical conductivity (EC) reflects the concentration and mobility of soluble ions in BC and is therefore closely associated with nutrient availability and ion exchange in soil. Like other physicochemical properties, EC is primarily controlled by feedstock composition and pyrolysis conditions, which determine the quantity and chemical form of mineral salts retained during carbonization [24,51].

Feedstock composition is the main source of EC variability because it determines the initial abundance of soluble minerals. Mineral-rich feedstocks, particularly manures and agricultural residues containing high concentrations of K, Ca, and Mg, generally produce BCs with higher EC than woody biomasses. This difference is evident even under identical pyrolysis conditions. Stella et al. [71] reported EC values of 1.31 dS m^{-1} for cabbage leaves, 0.59 dS m^{-1} for pea pods, and 0.23 dS m^{-1} for orange peels demonstrating that feedstock composition strongly influences the final ionic content of BC.

Pyrolysis temperature further modifies EC by concentrating soluble mineral salts as volatile organic compounds are progressively removed. Consequently, EC generally increases with thermal severity, although the magnitude of this increase depends on the mineral composition of the feedstock. Residence time has a comparatively smaller effect because it mainly promotes further carbonization without substantially changing the overall ionic content.

From an agronomic perspective, EC represents a balance between nutrient supply and salinity risk. Moderate EC favors the gradual release of K^+ , Ca^{2+} and Mg^{2+} improving soil fertility and reducing fertilizers requirements. However, excessively high EC may increase soil salinity and promote ionic imbalances, particularly in soils with low buffering capacity or under high BC application rates [72]. Therefore, EC should be interpreted together with feedstock type and soil characteristics when selecting BC for agricultural applications.

The comparative data summarized in Table 1 illustrates these contrasting responses. Agricultural and woody lignocellulosic feedstocks generally exhibit low to moderate EC values ($<5 \text{ dS m}^{-1}$), although EC increases progressively with pyrolysis temperature because of ash concentration. Nevertheless, important differences remain among lignocellulosic materials according to their mineral composition. For example, pistachio shell BC reaches 33.9 dS m^{-1} [64], whereas many woody residues remain below $2\text{--}3 \text{ dS m}^{-1}$, even after pyrolysis at $600\text{--}700^\circ\text{C}$ [3,50]. These results indicate that temperature alone cannot explain EC development; the initial mineral composition of the feedstock remains the dominant factor.

Animal and urban waste-derived BCs show a markedly different behavior. Their EC commonly exceeds 10 dS m^{-1} , reaching 23.75 dS m^{-1} in manure-derived BCs and 30.30 dS m^{-1} in algal biomass [70]. This consistently higher EC reflects the greater abundance of soluble ions, including K^+ , Na^+ , Ca^{2+} , Mg^{2+} , NH_4^+ , and phosphates species, which become concentrated during pyrolysis. Consequently, these materials can provide an immediate nutrient source but also present a greater risk of salt accumulation than lignocellulosic BCs. Overall, EC in lignocellulosic BCs mainly reflects gradual mineral enrichment during pyrolysis, whereas in animal- and waste-derived BCs, it is largely an intrinsic characteristic of the feedstock. This distinction should be considered when selecting BCs to improve soil fertility while minimizing salinity risks.

3.5. Bulk Density

Bulk density reflects the relationship between BC mass and the total volume it occupies, including pore spaces. As a structural property, it is closely linked to pore development and therefore influences soil aeration, water movement, and nutrient transport. Like other physicochemical properties, bulk density is primarily controlled by feedstock composition and pyrolysis conditions. BCs produced from woody lignocellulosic feedstocks generally exhibit lower bulk densities because their highly porous carbon matrix develops during pyrolysis, whereas animal- and waste-derived BCs tend to remain denser owing to their higher mineral and ash contents [26,73].

Feedstock composition explains much of the variability reported in the literature. Alburquerque et al. [73] measured bulk densities 0.740 g cm^{-3} for almond shell, 0.718 g cm^{-3} for olive stone, 0.655 g cm^{-3} for olive-tree pruning, 0.254 g cm^{-3} for pine woodchips, and 0.190 g cm^{-3} for wheat straw. Likewise, Usman et al. [74] reported value of 0.35 g cm^{-3} for *Conocarpus*-derived BC. These differences indicate that lignocellulosic composition, mineral content, and the original plant structure jointly determine the final density of BC.

Pyrolysis temperature generally decreases bulk density because devolatilization promotes micropore formation and increases the apparent volume of the material [36,75]. However, this response is not universal and depends on the balance between pore development, structural shrinkage, and mineral content. For example, BC produced from oil palm stones between 400 and 800 °C exhibited a 15.7% increase in porosity, accompanied by a 0.13 g cm^{-3} reduction in bulk density. At 900 °C, however, density increased again because structural sintering partially collapsed pore walls and consolidated polyaromatic structures.

Similar inconsistencies have been reported for other feedstocks. Rajkovich et al. [49] found bulk densities ranging from 0.65 and 0.10 g cm^{-3} in BCs produced from poultry litter with sawdust bedding, food waste, hazelnut shells, paper mill sludge, oak wood, pine wood, digested dairy manure, and corn stover between 300 and 600 °C, without observing a consistent relationship between pyrolysis temperature and density. Poultry manure-derived BCs ($0.65\text{--}0.52 \text{ g cm}^{-3}$) consistently showed the highest bulk densities and lowest porosities, reflecting their greater inorganic content and limited micropore development. Together, these studies indicate that feedstock composition often exerts a stronger influence on bulk density than temperature alone.

Bulk density is also closely associated with structural properties. BCs exhibiting high SBET and pore volume, particularly those produced from agricultural and woody feedstock at 600–800 °C, generally show lower bulk densities because extensive micropore formation reduces the apparent density of the carbon matrix. This relationship agrees with Suliman et al. [36], who reported that greater porosity is accompanied by lower bulk density as cellulose and lignin degradation progressively generate a highly porous structure. In contrast, animal- and urban waste-derived BCs, characterized in Table S1 by lower SBET, lower pore volumes, and higher pH and EC values, generally maintain denser structures because mineral phases limit pore development. These structural differences have direct agronomic implications. Low-density BCs improve soil aeration, reduce compaction, and facilitate water infiltration, whereas denser materials contribute more to aggregate stability and water retention [36]. Consequently, bulk density indirectly regulates nutrient availability by modifying water flow, ion transport, microbial habitat, and cation retention within the soil matrix.

Overall, bulk density reflects the balance among devolatilization, pore formation, structural shrinkage, and mineral accumulation during pyrolysis. The relative contribution of each process depends strongly on feedstock composition, explaining why increasing py-

rolysis temperature does not always produce the same structural response across different biomass types [76,77].

3.6. Cation Exchange Capacity

Cation exchange capacity (CEC) is one of the most important agronomic properties of BC because it governs the retention, exchange, and gradual release of essential cations, including NH_4^+ , K^+ , Ca^{2+} , and Mg^{2+} . It reflects the density of negatively charged surface sites and is mainly controlled by feedstock composition, oxygen-containing functional groups, mineral composition, and the degree of carbonization [78–80]. Its agronomic relevance is illustrated by Amazonian anthropogenic soils, where the accumulation of pyrogenic carbon contributes to both high fertility and elevated CEC [81]. Depending on feedstock and production conditions, BC CEC commonly ranges from 20.1 to 75.8 $\text{cmol}^+ \text{kg}^{-1}$, [82].

Among the production variables, pyrolysis temperature has the greatest influence on CEC because it regulates the preservation or loss of oxygen-containing functional groups. BCs produced at 350–450 °C generally exhibit the highest CEC values because carboxylic, hydroxyl, and phenolic groups remain abundant, providing negatively charged sites for cation adsorption [48,83,84]. Accordingly, numerous studies have reported a positive relationship between the O/C ratio and CEC, indicating that less carbonized BCs retain a greater density of exchange sites [82,85]. Likewise, Duman and Yanik [82] observed that higher volatile matter contents are associated with higher CEC values, although this relationship is not exclusive and also depends on the structure of the precursor.

Increasing pyrolysis temperature usually decreases CEC because dehydroxylation and aromatic condensation progressively remove surface oxygen functionalities [49,57,60,86]. This trend is accompanied by lower O/C ratios and weaker C–O signals in FTIR spectra. However, the response is not universal and depends strongly on feedstock composition [82]. Wijitkosum [14] observed that CEC decreased with temperature in chicken manure- and eucalyptus-derived BCs, whereas coffee husk BC showed the opposite trend, which was attributed to the concentration of alkaline minerals during pyrolysis. Similarly, Domingues et al. [48] reported that coffee husk BC increased from 70 to 73 $\text{cmol}^+ \text{kg}^{-1}$ between 350 and 750 °C. These contrasting observations indicate that mineral enrichment can partially compensate for the loss of oxygen-containing functional groups in some feedstocks. CEC is also influenced by solution pH because deprotonation of surface functional groups increases the density of negative charges available for cation exchange. Consequently, BCs produced at lower temperatures usually exhibit greater pH-dependent CEC, whereas highly carbonized materials show a weaker response because many reactive functional groups have already been removed.

Feedstock composition further contributes to the wide variability reported for BC CEC. Mineral-rich agricultural and animal residues frequently exhibit the highest values. Poultry manure BC reaches 75 $\text{cmol}^+ \text{kg}^{-1}$ at 400 °C [51], corn straw 68.6 $\text{cmol}^+ \text{kg}^{-1}$ at 500 °C [83] and wheat BC 54.8 $\text{cmol}^+ \text{kg}^{-1}$ at 550 °C [87]. Even higher values have been reported for rice husk (111 $\text{cmol}^+ \text{kg}^{-1}$ at 400 °C) [88], greenhouse residues (109.5 $\text{cmol}^+ \text{kg}^{-1}$), and oak wood (105.8 $\text{cmol}^+ \text{kg}^{-1}$) between 400 and 450 °C [89]. non-woody BCs combining high ash contents with alkaline pH exhibit CEC values of up to 37 $\text{cmol}^+ \text{kg}^{-1}$ while maintaining high water-retention capacity, demonstrating that mineral phases and surface functionality jointly contribute to cation exchange [90].

From an agronomic perspective, BCs produced at intermediate pyrolysis temperatures generally provide the most favorable balance between structural stability and surface functionality. The application of moderately alkaline BCs (pH 7.3–9.2) produced between 500 and 650 °C improves nutrient retention, increases soil CEC, and supplies essential macronutrients such as K, Ca, and Mg, thereby promoting microbial activity and organic

matter stability [91]. In addition, macronutrient-rich BCs can reduce N losses through NH_3 volatilization and denitrification, improving fertilizer-use efficiency [58]. Overall, these findings indicate that CEC is governed by the interaction among surface functionality, mineral composition, and thermal severity, with the highest values generally occurring at intermediate pyrolysis temperatures, where oxygen-containing functional groups and an active mineral fraction are simultaneously preserved.

The data presented in Table S1 support these trends. In agricultural and woody lignocellulosic feedstocks, CEC generally reaches moderate to high values at intermediate temperatures (400–600 °C), where carboxyl and phenolic groups remain sufficiently abundant to provide negatively charged exchange sites. Some agricultural feedstocks exceed 80–100 $\text{cmol}^+ \text{kg}^{-1}$, whereas woody materials typically range from 20 to 65 $\text{cmol}^+ \text{kg}^{-1}$ [50]. At temperatures ≥ 700 °C, CEC frequently stabilizes or decreases because progressive deoxygenation and aromatic condensation reduce the abundance of reactive surface groups. Residence time plays a secondary role by promoting structural stabilization, although prolonged carbonization may further reduce the density of exchange sites.

Animal- and urban waste-derived BCs exhibit different behaviors. Their CEC may also reach 60–75 $\text{cmol}^+ \text{kg}^{-1}$ in some manures and sludges [51]. However, unlike lignocellulosic BCs, these values result not only from carbon surface chemistry but also from exchangeable mineral phases associated with their ash-rich composition. Thus, similar CEC values may arise from different mechanisms depending on feedstock composition. From an agronomic perspective, high CEC enhances the retention of K^+ , Ca^{2+} , Mg^{2+} , and NH_4^+ , reducing nutrient leaching and improving fertilizer-use efficiency. Overall, BCs produced at intermediate temperatures provide the most favorable balance between structural stability and exchange capacity, promoting nutrient storage and gradual nutrient release in soil.

3.7. Chemical Nature

The chemical nature of BC governs its structural stability, surface reactivity, and capacity to retain and release macronutrients in soil. One of its defining characteristics is the formation of condensed aromatic structures during pyrolysis, which provide high chemical stability and resistance to microbial degradation, allowing BC to persist in soil over long periods [92,93]. During pyrolysis, biomass undergoes dehydration, decarboxylation, and aromatic condensation, transforming aliphatic and oxygenated compounds into highly conjugated carbon structures [32]. As temperature increases, H, O, and N contents decline together with volatile matter, increasing structural condensation while reducing surface polarity [58,83]. This transformation progressively removes reactive surface functionalities, particularly carboxyl, hydroxyl, and carbonyl groups, which are largely responsible for cation exchange and interactions with NH_4^+ , K^+ , Ca^{2+} , and Mg^{2+} [84].

The H/C and O/C atomic ratios are widely used to describe these structural changes. The H/C ratio reflects the degree of carbon condensation, whereas the O/C ratio indicates the abundance of polar surface functionalities and, consequently, BC hydrophilicity and chemical reactivity [39]. BCs produced at high pyrolysis temperatures (>600 °C) generally exhibit low H/C and O/C ratios, indicating highly condensed and chemically stable structures but lower ionic retention capacity. By contrast, BCs produced at intermediate temperatures (350–500 °C) preserve a greater proportion of surface functional groups, favoring nutrient adsorption, exchange, and retention. Therefore, the agronomic performance of BC depends on balancing long-term structural stability with sufficient surface functionality to maintain nutrient interactions [86].

The O/C and H/C atomic ratios reported in Table S1 consistently reflect the degree of carbonization and structural evolution of BC as a function of feedstock and thermal severity. In lignocellulosic agricultural biomass, increasing the temperature from 300–400 °C to

600–800 °C induces a marked decrease in O/C, from values close to 0.70–1.00 to <0.20, and in H/C, from ~1.0–1.2 to <0.30, as observed in sunflower straw and tomato green waste treated up to 700 °C.

The data presented in Table S1 clearly illustrate these trends. In agricultural lignocellulosic feedstocks, increasing pyrolysis temperature from 300–400 °C to 600–800 °C reduces O/C ratios from approximately 0.70–1.00 to below 0.20 and H/C ratios from about 1.0–1.2 to below 0.30, as reported for sunflower straw, tomato green waste at 700 °C [47], orange pomace at 600 °C [70], and rice husk at 650 °C [94]. Woody feedstocks follow a similar pattern. For example, *Acer velutinum* branches exhibited H/C and O/C ratios below 0.30 and 0.20, respectively, after pyrolysis at 700 °C [95], confirming the progressive development of highly condensed carbon structures. This structural evolution is consistently accompanied by lower BC yields, which typically decrease from more than 60–80% at low temperatures to less than 30–40% at 700–800 °C because of progressive devolatilization.

Animal- and urban waste-derived BCs exhibit a different evolution. Compared with lignocellulosic feedstocks, changes in H/C and O/C are generally less pronounced because their higher mineral contents and lower lignin proportions reduce the extent of structural carbon rearrangement during pyrolysis. Poultry and bovine manure BCs produced between 350 and 750 °C typically exhibit O/C ratios of 0.25–0.49 and H/C values above 0.30 [25,48]. Similarly, sewage sludge BC may retain broad O/C (0.01–0.95) and H/C (0.03–1.01) ranges even after high-temperature pyrolysis [96]. These contrasting responses indicate that identical thermal conditions do not produce the same degree of carbonization across different feedstocks. Consequently, lignocellulosic BCs generally maximize long-term carbon stability, whereas mineral-rich feedstocks preserve greater chemical functionality through both residual surface groups and inorganic phases. Overall, the combined evolution of H/C, O/C, and BC yield demonstrates that feedstock composition and pyrolysis temperature jointly determine the balance between structural stability, surface reactivity, and nutrient retention.

3.8. Adsorption, Desorption, and Nutrient-Source Potential of Biochar

Nutrient adsorption and desorption govern the capacity of BC to function simultaneously as a nutrient sink and a nutrient source. These complementary processes regulate the retention, gradual release, and bioavailability of macronutrients (N, P, K, S, Ca, and Mg) in soil. In their role as adsorbents, BCs can be classified into two main types: (1) heteroatom-rich BCs (O, N, S, and P), in which polar interactions predominate, including hydrogen bonding, ion-dipole interactions, and dipole-dipole interactions; and (2) highly carbonized BCs, in which hydrophobic, π - π , and anion-exchange interactions dominate [34,97,98].

Adsorption efficiency depends primarily on feedstock type and pyrolysis temperature. BCs produced at low temperatures (300–450 °C) preserve oxygen-containing functional groups (-OH, -COOH, and -C=O), which are responsible for cation retention through complexation and electrostatic forces. In contrast, BCs produced at high temperatures (>600 °C) exhibit greater aromaticity, lower polarity, and loss of acidic groups, which reduces their ionic adsorption capacity but may favor mineral precipitation and anion retention through surface exchange [14,24,99]. For example, Ippolito et al. [100] demonstrated that a grass-derived BC produced at 250 °C reduced nutrient leaching more effectively than the material carbonized at 650 °C, due to the preservation of higher CEC and a more active surface.

The adsorption-desorption process in BCs is dynamic and reversible. After initial adsorption, nutrients can be gradually released into the soil solution depending on pH, ionic strength, ion competition, water availability, and microbial activity [101,102]. Desorption occurs through the rupture of weak physical or electrostatic bonds between the ion and the BC surface, allowing gradual nutrient release. This equilibrium underpins the

behavior of BC as a slow-release and nutrient-buffering amendment, capable of supplying nutrients according to crop demand and soil conditions [103,104]. The molecular-level mechanisms responsible for these interactions are summarized in Figure 4, which illustrates the main adsorption, retention, and release pathways governing macronutrient dynamics on BC surfaces.

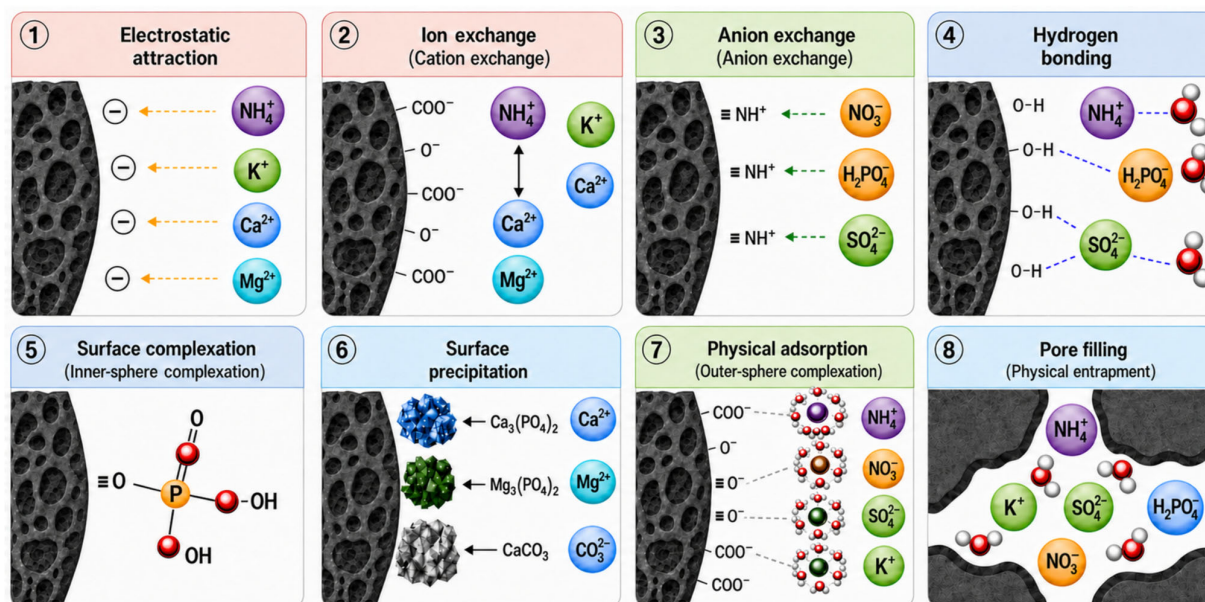


Figure 4. Molecular-level mechanisms governing macronutrient adsorption, retention, and release on biochar surfaces.

As illustrated in Figure 4, nutrient retention and release are governed by four main mechanisms: (I) cation exchange, dominant for ions such as NH_4^+ , K^+ , Ca^{2+} , and Mg^{2+} , facilitated by the presence of carboxylic and phenolic groups; (II) anion exchange, associated with nitrogen-containing functional groups, such as pyridinic, pyrrolic, and oxonium groups, which allows the reversible retention of anions such as NO_3^- and H_2PO_4^- ; (III) surface precipitation, promoted in alkaline BCs rich in Ca, Mg, or K; and (IV) porous diffusion and physical entrapment, favored by high surface area and hierarchical pore structure [11].

Desorption largely depends on the strength and reversibility of nutrient–surface interactions. Nutrients retained through weak interactions, such as van der Waals forces or hydrogen bonding, are rapidly released, whereas those associated with specific sites, including carbonyls, phenols, or metal–oxygen complexes, exhibit slower and more sustained release [105]. Therefore, the balance between strong and reversible adsorption defines the effectiveness of BC as an active nutrient reservoir.

BC aging alters both adsorption and desorption by progressively increasing surface oxidation. During aging, exposure to oxygen, moisture, and microorganisms generates new carboxylic and carbonyl groups, increasing negative surface charge and CEC [102]. In parallel, water retention and gradual nutrient release are intensified, processes that enhance soil fertility and fertilizer-use efficiency. In soil, the effect of BC on nutrient retention and leaching varies depending on BC properties, including biomass nature, pyrolysis temperature, hydrophobicity, and aging, as well as the amount applied and soil properties, such as texture, pH, and the chemical species of the nutrients present [106].

The beneficial effects of BC on plant nutrition cannot be attributed to a single mechanism. Instead, they result from the combined contribution of several processes, including: (I) the native nutrient content of BC; (II) improvements in soil physical and chemical prop-

erties, including bulk density, pH, and water and nutrient retention; (III) vigorous root development; (IV) promotion of microbial activity and function; (V) stimulation of plant growth and microbial communities, including rhizobacteria; (VI) increased nutrient mineralization from soil organic matter; and (VII) reductions in nutrient losses [5]. Thus, BC functionality depends not only on its surface chemistry but also on its dynamic interaction with soil and its evolution over time.

Soil, plant, and environmental responses to BC application depend largely on BC composition and properties, as well as on plant species and the environmental and experimental conditions under which they are evaluated [107]. These properties are directly determined by the feedstock used and pyrolysis depends not only on its surface chemistry but also on its dynamic interaction with soil and its evolution over time. BCs derived from agricultural biomass exhibit high contents of aromatic carbon, attributable to the high proportion of lignin and cellulose in these feedstocks, conferring greater structural stability and resistance to microbial decomposition [85]. Animal waste-derived BCs are characterized by higher proportions of labile organic and inorganic compounds, resulting in elevated ash contents. Likewise, BCs obtained through slow pyrolysis retain larger amounts of aliphatic compounds, labile carbon, and nutrients, making them particularly suitable for agricultural soil management [108]. In contrast, BCs produced by fast pyrolysis exhibit a higher degree of aromaticity and fixed carbon content, making them more suitable for strategies aimed at soil carbon sequestration [5,109]. These contrasting characteristics highlight the trade-off between nutrient availability and carbon stability. Slow pyrolysis favors nutrient preservation and soil fertility, whereas fast pyrolysis enhances carbon stabilization and long-term sequestration.

The comparative data summarized in Table 2 reveals clear differences in nutrient-source potential among biomass categories. In general, dry-basis ash content increases with pyrolysis temperature for all types of BCs, reflecting the concentration of the inorganic fraction as volatile organic compounds are progressively lost. Particularly high ash contents are observed in mineral-rich feedstocks, such as rice husk (91.2%) and rice straw (52.0%) [88]. In addition, urban waste-derived BCs are increasingly recognized as relevant materials for nutrient recovery and circular bioeconomy strategies, particularly after upgrading processes that enhance porosity, surface functionality, and the recovery of nutrients such as P, K, Mg, and Ca [89].

Regarding elemental composition, the major elements C, H, O, N, and S account for more than 60% of BC composition, followed by K, P, Na, Mg, and Ca, and, in lower proportions, by Mn, Si, Fe, Al, Cu, and Zn [110,111]. Regardless of the feedstock, carbon is the predominant element, with woody residues showing the highest percentages, as in the case of white Albizia wood (92.3%) [112]. Nitrogen content in BCs is generally below 5%, reaching 4.4% in chicken manure [113]. Hydrogen and oxygen contents are higher than nitrogen contents, with maximum values of 5.6 and 42.3 wt.%, respectively, reported for poultry litter [51]. In general, sulfur contents are low and may even be undetectable by the analytical techniques used; however, values of 2.3% have been reported for *Conocarpus* at 200 °C [114] and 2.1% for date palm at 300 °C [65]. In these cases, sulfur percentage decreases with increasing pyrolysis severity, indicating progressive volatilization at higher temperatures.

Regarding phosphorus, substantial amounts remain in BCs after the pyrolysis of feedstocks such as wood, straw, manures, and agricultural biomass [115]. When comparing different biomass types, animal wastes exhibit the highest P contents, with goat manure standing out at 5.3 wt.% at 600 °C and turkey manure at 3.7 wt.% at 700 °C. Furthermore, increasing the carbonization temperature up to 700 °C promotes enrichment in P, as well

as in Ca, Mg, K, Mn, Na, Si, Fe, Al, Cu, and Zn; however, phosphorus begins to partially volatilize between 700 and 800 °C [116].

With respect to alkaline earth elements, calcium content is usually slightly higher than that of potassium and sodium, which is favorable for soil structure, since a high proportion of monovalent relative to divalent cations can negatively affect structural stability [117]. Magnesium content varies depending on biomass: it is generally lower than calcium, although in biomasses such as rice husk [118] and grape pomace [119], it may exceed calcium; in contrast, in materials such as urban wastes [89], poultry litter [89], and wheat straw [120], magnesium is lower than potassium. Finally, the contribution of calcium and magnesium from BCs directly affects soil pH, making them potentially useful amendments for infertile and sandy soils [121].

Taken together, Table 2 shows that feedstock type is the primary determinant of the nutrient-source potential of BC, whereas pyrolysis temperature mainly controls nutrient concentration, stability, and chemical form. Woody BCs are characterized by high carbon contents and relatively low nutrient concentrations, making them more relevant for carbon stabilization than for direct nutrient supply. Agricultural residues generally provide moderate to high levels of mineral nutrients, particularly K, while animal waste-derived BCs stand out because of their greater P, Ca, and K contents. Aquatic biomass-derived BCs, including those produced from microalgae and macroalgae, may also exhibit high N and mineral contents due to their protein- and salt-rich composition; species such as *Chlorella* sp. and *Spirulina* sp. can reach N contents above 5%, whereas macroalgae such as *Undaria pinnatifida* and *Enteromorpha prolifera* contain appreciable amounts of K and Ca, suggesting their potential as nutrient sources in agricultural soils [122].

These differences indicate that BCs derived from distinct biomass categories should not be regarded as interchangeable amendments. Instead, they provide different agronomic functions depending on their dominant nutrient composition and mineral characteristics. Animal-derived BCs are particularly suitable as multi-nutrient amendments and liming materials, whereas agricultural and aquatic BCs may be preferable for correcting specific nutrient deficiencies, especially those related to K and secondary macronutrients. In contrast, woody BCs are more appropriate for improving nutrient retention, reducing leaching losses, and enhancing long-term soil carbon storage. Urban-waste BCs also offer opportunities for nutrient recycling, particularly for P and micronutrients, although their use requires careful assessment of potential contaminants. Overall, the data reinforce the dual role of BC as both a nutrient source and a nutrient-regulating material. However, agronomic performance cannot be inferred solely from total nutrient concentrations. The most effective BCs are those whose nutrient composition and physicochemical characteristics match the limitations of the target soil and the nutritional requirements of the cropping system. Consequently, biomass selection should be guided by the intended agronomic function, supporting the conceptual framework proposed in this review that links biomass type and pyrolysis conditions with soil macronutrient dynamics.

Table 2. Conceptual framework linking biomass type, nutrient composition, and agronomic applications of biochars, derived from the dataset reported in Supplementary Table S2.

Biomass Category	Dominant Nutrients	Representative Feedstocks	Main Agronomic Use	Recommended Agronomic Applications	Key Limitation	Reference
Agricultural biomass	Usually enriched in K; moderate Ca, Mg, Si and variable P.	Rice husk, wheat straw, corn straw, cocoa husk, grape pomace, bagasse, peanut shell.	K amendment and gradual nutrient release.	K-deficient soils, sandy soils and integrated nutrient management.	Strong feedstock-dependent variability in nutrient composition.	[119,123]

Table 2. Cont.

Biomass Category	Dominant Nutrients	Representative Feedstocks	Main Agronomic Use	Recommended Agronomic Applications	Key Limitation	Reference
Woody biomass	Low N, P and K; occasional Ca and Mg; high stable C.	Pine chips, oak wood, Douglas fir, bamboo, softwoods, hardwoods.	Nutrient retention and carbon sequestration.	Improving nutrient-use efficiency, reducing nitrate leaching and enhancing soil structure.	Limited direct nutrient supply and low fertilization potential.	[73,114,124]
Animal waste	High P, K, Ca and Mg; moderate to high N.	Poultry litter, poultry manure, pig manure, turkey manure, dairy manure, goat manure.	Multi-nutrient fertilizer and liming material.	Nutrient-poor soils, acidic soils and degraded lands.	Potential salinity, NH ₃ volatilization and excess P accumulation.	[51,123,125]
Urban waste	High P and micronutrients (Fe, Zn, Cu, Mn); often high Ca.	Sewage sludge, food waste, food industrial sludge, textile sludge.	P recycling and micronutrient recovery.	P-deficient soils and circular nutrient management.	Potential accumulation of heavy metals and organic contaminants.	[123,126,127]
Aquatic biomass	Relatively high N, Ca, Mg and S; variable P and K.	<i>Chlorella</i> sp., <i>Spirulina</i> sp., <i>Enteromorpha prolifera</i> , <i>Undaria pinnatifida</i> .	Liming effect and gradual nutrient supply.	Acidic or degraded soils requiring base cations.	Variable composition and possible salinity concerns.	[55,122,128]

3.9. Biochar Aging and Oxidation: Time-Dependent Controls on Soil Function and Nutrient Retention

BC aging does not produce a single or uniform response in soil. Instead, its effects vary with exposure time, application strategy, dose, feedstock type, pyrolysis conditions, and soil properties. Long-term field studies show that aged BC can maintain significant effects on microbial communities and C and N cycling, although the magnitude and direction of these responses differ among production systems. Nan et al. reported that 10 years of continuous BC application in paddy soil increased soil pH and altered bacterial and archaeal diversity, with pH acting as a major regulator of nitrification potential and methanotrophy-related functions. By contrast, Mao et al. [129] evaluated a single BC application after 12 years in an acidic subtropical forest soil and observed increases in extractable organic C and N together with greater bacterial network complexity as BC dose increased. However, fungal diversity declined. These contrasting responses indicate that the biological effects of aged BC depend not only on aging itself but also on soil type, application frequency, and application rate.

Physical changes during aging also exhibit contrasting patterns. Jiang et al. [130], Ye et al. [131], and Barbosa et al. [132] show that aging can improve some BC functions while reducing others. Jiang et al. [130] showed that BC increased total porosity, saturated hydraulic conductivity, field capacity, and available water capacity while reducing soil bulk density. These improvements were greatest during the first years after application and gradually weakened over time. Ye et al. [131] provided a mechanistic explanation for this trend, demonstrating that biotic colonization and abiotic surface coverage increased crack width and promoted particle fragmentation. Although fragmentation exposes internal pores and reactive surface groups, it may also reduce the structural integrity of BC particles. Barbosa et al. [132] further showed that this response depends on feedstock and pyrolysis conditions. Sewage sludge-derived BCs were more susceptible to C loss and oxidative transformation but retained biofertilizer potential because of their higher initial N content and

reactive surfaces. In contrast, wheat straw-derived BCs were more resistant to degradation while continuing to develop greater porosity. These findings demonstrate that aging should not be regarded solely as a degradation process because it may simultaneously reduce structural integrity while enhancing surface reactivity and nutrient-related functionality.

Aging also influences nutrient retention and controlled nutrient release through multiple mechanisms. Wang et al. [133] showed that repeated BC application over eight years increased total N uptake, fertilizer-N recovery, and the retention of fertilizer-derived N within the 0–80 cm soil profile, thereby reducing the risk of deep N leaching. Liang et al. [134] reported that BC-based slow-release phosphate fertilizers promoted the formation of stable inorganic P fractions, supporting a more sustained supply of plant-available P. Negi et al. [135] found that BC enhanced microbial colonization and improved redox stratification in vertical-flow constructed wetlands, facilitating N removal in a liquid treatment system. Although these observations were obtained outside conventional agricultural soils, they provide complementary evidence that BC can function as an effective microbial support material. Collectively, these studies indicate that aging and engineered modification do not simply alter BC properties over time; rather, they regulate nutrient dynamics through changes in surface chemistry, pore structure, microbial colonization, and nutrient speciation. Consequently, the agronomic performance of aged BC depends on the interaction between these transformations and the environmental conditions under which the material is applied.

4. Effect of Biochar on Nutrient Dynamics in Soil

4.1. Nitrogen

4.1.1. Microbial Nitrogen Transformations

Nitrogen (N) is the macronutrient that most commonly limits crop productivity, particularly in cold and temperate terrestrial ecosystems. In soil, most N occurs in organic forms that must first be mineralized to release ammonium, which can subsequently be oxidized to nitrate through microbial nitrification [136]. Both NH_4^+ and NO_3^- are available for plant uptake and therefore determine nitrogen-use efficiency [137]. Denitrification reduces nitrate under anoxic conditions to gaseous products (N_2 , NO, and N_2O), which are ultimately released into the atmosphere. These transformations are mediated by distinct microbial groups. Bacteria and archaea primarily perform ammonia oxidation, nitrite oxidation, and classical denitrification, whereas some heterotrophic bacteria and fungi contribute to heterotrophic nitrification and fungal denitrification. Unlike most denitrifying bacteria, several fungi lack the *nosZ* gene and therefore frequently terminate denitrification at N_2O rather than completing its reduction to N_2 [138].

Rather than acting on a single microbial process, BC modifies the environmental conditions that regulate the entire soil N cycle. Stevenson and Cole [136], Berglund et al. [139], Gundale and DeLuca [140], Cayuela et al. [141], and Meier et al. [115] demonstrated that BC influences ammonification, nitrification, denitrification, and biological N fixation. These responses arise from the interaction between BC properties and soil conditions, particularly pH, oxygen diffusion, redox status, and the availability of C and N substrates. Consequently, BC may promote (I) organic N mineralization [142]; (II) nitrification through stimulation of ammonia-oxidizing microorganisms [140,143]; and (III) reduced denitrification under well-aerated conditions [141,144]. At the same time, BC retains ammoniacal N, reducing NH_3 volatilization [137,145], while its labile carbon fraction stimulates microbial immobilization, temporarily incorporating inorganic N into microbial biomass [146,147]. These concurrent processes explain why BC may simultaneously enhance N retention while modifying microbial N transformations.

The magnitude of these effects depends strongly on feedstock composition and the duration of soil–BC interaction. Manure-derived BCs generally stimulate mineralization more effectively than plant-derived BCs because of their higher initial N content [103,143]. Time also plays an important role. Shortly after application, BC commonly increases mineralization rates by supplying bioavailable carbon that stimulates microbial activity [147–150]. As aging progresses, however, mineralization tends to decline because organic compounds become increasingly adsorbed onto BC surfaces, reducing their accessibility to microorganisms [148–150].

Nitrogen immobilization is likewise controlled by the interaction between BC properties and soil characteristics. Microorganisms may assimilate inorganic N associated with fresh BC, temporarily reducing its availability to plants. This response is particularly evident in systems with C/N ratios above 32, where microbial immobilization predominates [146,151]. Higher volatile matter contents, representing the more labile aliphatic fraction of BC, are also associated with greater immobilization potential [152]. Woody BCs, characterized by greater recalcitrance, generally favor this process [153]. Nevertheless, improved soil porosity and lower bulk density simultaneously stimulate microbial activity. Consequently, whether nitrification increases or decreases ultimately depends on N availability and soil conditions rather than on BC alone.

Nitrification illustrates this interaction particularly well. Improved aeration resulting from greater soil porosity favors the activity of nitrifying microorganisms [143,154,155], increasing the conversion of NH_4^+ to NO_3^- under aerobic conditions [143]. This effect is especially pronounced in acidic soils because BC increases soil pH, alleviating one of the main limitations to nitrification [141], although their effects in alkaline soils have not yet been clearly established [141]. However, the response is not always positive. BC produced during wildfires may enhance nitrification by adsorbing phenolic compounds that inhibit nitrifying microorganisms [139]. Conversely, fresh BC may temporarily suppress nitrification because volatile compounds such as acetaldehyde, α -pinene, β -pinene, pinene, and ethylene inhibit nitrifying bacteria. Clough et al. [156] identified α -pinene as one of the compounds responsible for this inhibitory effect. These contrasting observations indicate that nitrification depends not only on BC properties but also on its degree of aging and the persistence of volatile compounds after production.

A similar complexity characterizes denitrification and N_2O emissions. Numerous studies have shown that BC reduces N_2O emissions [157–159], although current evidence indicates that this effect results from modifications of the environmental controls regulating N_2O production and consumption rather than from suppression of a single microbial pathway [138]. Proposed mechanisms include (I) binding of N_2O to metal cations present in BCs [141]; (II) adsorption of soil organic matter, which decreases the bioavailability of N_2O -generating substrates and microbial activity [148]; (III) the neutralizing effect of BCs, which influences the synthesis and activity of the enzyme N_2O reductase [141,160]; and (IV) improved soil aeration, which suppresses denitrification under oxygen-rich conditions [161]. BC may also alter oxygen diffusion, redox microsites, C and N availability, trace-metal availability, and electron-transfer processes, thereby determining whether denitrification terminates at N_2O or proceeds to N_2 [138].

BC also promotes biological N fixation by improving the habitat of both free-living and symbiotic N-fixing microorganisms [103,162]. Improved soil structure, greater nutrient availability, and enhanced nodulation favor *Rhizobium* development [143]. In addition, BC can adsorb signaling molecules such as Nod factors and flavonoids, strengthening communication between the host plant and its microbial symbionts [163]. Overall, the available evidence indicates that BC does not regulate a single step of the N cycle. Instead,

it modifies the physical, chemical, and biological conditions that collectively determine nitrogen transformation, retention, and loss in soil.

4.1.2. Nitrogen Bioavailability

Nitrogen bioavailability in BC-amended soils is controlled by the interaction between BC properties, the C/N ratio, pyrolysis conditions, application rate, and soil characteristics. Fresh BCs with low C/N ratios generally stimulate mineralization, increasing inorganic N availability and modifying the balance between plant uptake and microbial immobilization [146,147,149,164]. This response is strongly influenced by application rate. For example, adding 1 or 2% (*w/w*) of *Quercus ilex* L. BC produced at 600 °C to an acidic sandy loam initially increased the potentially mineralizable N fraction in proportion to the application rate. After incubation, however, the readily mineralizable N pool declined more rapidly at the higher application rate, indicating faster depletion through enhanced mineralization [147].

Under appropriate application rates, BC generally increases both total and plant-available N while reducing N losses. Its high porosity and BET specific surface area enhance N retention and limit leaching [165], leading to reported increases of 4.7–32.3% in total N and 11.5–58.9% in available N, depending on application rate [166]. Greater BC additions may also increase microbial biomass N by improving carbon availability and stimulating microbial growth, although this response varies with soil texture, microbial abundance, and feedstock type [167–169]. Interestingly, several studies reported lower soil NO_3^- concentrations (2.6–12.5%) despite increases in total and available N. This apparent contradiction is explained by greater root N uptake and improved soil aeration, which increased wheat N uptake by 15.3–65.2% [167].

Not all studies, however, report increased N availability. Schomberg et al. [170] found only limited changes in mineralization following the application of BCs derived from poultry litter, pecan shell, peanut hull, switchgrass, and CQuest. Their results showed that the amount of N incorporated into recalcitrant BC structures depended on both feedstock type and pyrolysis temperature. In particular, poultry litter-, pecan shell-, and peanut hull-derived BCs stabilized relatively small amounts of N at higher pyrolysis temperatures, a response associated with increased pH and ash content. These observations indicate that greater alkalinity does not necessarily translate into higher N retention. Nitrogen retention should therefore be interpreted as the result of several interacting processes rather than a single mechanism. Mineralization, microbial immobilization, soil aeration, root uptake, and the adsorption–desorption behavior of NH_4^+ and NO_3^- collectively determine the amount of plant-available N and the potential for N leaching. The adsorption and desorption mechanisms controlling these inorganic N forms are discussed in Sections 4.1.3 and 4.1.4, respectively.

BC effects on N_2O emissions show a similarly complex behavior. Feedstock composition, pyrolysis temperature, C/N ratio, application rate, soil type, and N fertilization all influence the magnitude of N_2O mitigation [141]. Hatton et al. [160] that manure-derived BCs, particularly those produced from poultry manure, initially generated higher nitrification–denitrification rates and greater N_2O emissions than wood-derived BCs because of their higher N content. After four months of soil contact, however, N_2O emissions decreased below those of the untreated control regardless of feedstock. The same BC also produced different responses depending on the initial soil N content, consistent with the observations of Liu et al. [171]. In addition, BCs rich in Fe and Mn may catalyze the reduction of N_2O to N_2 , providing an additional mechanism for mitigating greenhouse gas emissions [103]. Conversely, other studies reported no significant effect of BC on N_2O production [172–174], whereas others observed increased emissions in dry soils with

low organic C contents [159,175]. These contrasting results indicate that N_2O mitigation depends more on soil conditions and BC characteristics than on BC application alone.

Similar trade-offs have been reported for crop productivity. Although BC frequently reduces N_2O emissions, this benefit does not always translate into greater crop yields. He et al. [176] reported average reductions of 15.65% in paddy soils and 11.23% in upland soils, mainly attributed to stronger NH_4^+ and NO_3^- retention, lower substrate availability for denitrifiers, and improved soil aeration. However, these same mechanisms may temporarily reduce plant-available N during the early stages of crop growth. Moreover, highly alkaline and ash-rich BCs increased NH_3 volatilization by an average of 14.12%, indicating that reductions in N_2O emissions may shift part of the N loss pathway toward NH_3 volatilization rather than completely preventing N losses.

These interactions help explain the variable crop responses reported in the literature. Zhang et al. [177] showed that high C/N ratios and the recalcitrant carbon structure of BC promote microbial N immobilization, temporarily restricting N availability for plants. Consequently, BC may improve environmental performance while producing smaller yield increases than nutrient-rich amendments such as manure or biofertilizers. Overall, the available evidence demonstrates that BC should not be regarded as a universal strategy for improving N bioavailability. Instead, its effectiveness depends on the interaction among feedstock type, pyrolysis conditions, soil properties, initial N status, and management practices. Co-application with controlled-release N fertilizers, composting, or BC aging may help minimize temporary N immobilization and NH_3 losses.

4.1.3. Ammonium Adsorption and Desorption

Ammonium in soil originates from the mineralization of organic matter as well as from fertilizer application and industrial ammonia emissions. Under aerobic conditions, nitrifying microorganisms oxidize NH_4^+ first to nitrite and subsequently to nitrate, a highly mobile form that is readily transported through the soil profile. In contrast, NH_4^+ can be retained within the soil exchange complex, although under alkaline conditions part of the ammoniacal N may be lost through NH_3 volatilization [117].

The retention of NH_4^+ by BC is governed by several complementary mechanisms rather than by a single adsorption process. In soils with low cation exchange capacity, BC enhances ammonium retention through electrostatic exchange between NH_4^+ and negatively charged oxygen-containing surface functional groups [178]. Hale et al. [179] reported distribution coefficients (K_d) of approximately 100 L kg^{-1} for coffee husk- and corn cob-derived BCs, indicating relatively weak but reversible electrostatic adsorption, a trend consistent with the observations of Aghoghovwia et al. [178].

Besides cation exchange, acid–base interactions also contribute to NH_4^+ retention. Ammonia (NH_3) can behave as both a Brønsted and Lewis base, whereas NH_4^+ interacts with acidic surface groups, particularly carboxylic functionalities, leading to the formation of ammonium salts or amide-like surface species. These interactions contribute to the hysteresis frequently observed during NH_4^+ desorption [157]. However, their relative importance remains uncertain because only a weak correlation ($R^2 = 0.31$) has been reported between NH_4^+ adsorption and the O/C ratio [178]. Additional interactions have been attributed to hydrogen bonding with aromatic domains and hydrophobic regions of the carbon matrix [79]. Accordingly, BCs with lower H/C ratios, indicative of greater aromatic condensation, generally exhibit stronger affinity for NH_4^+ [178]. FTIR analyses further demonstrated the involvement of alkyl ($-\text{CH}_2-$) and carbonyl ($\text{C}=\text{O}$) groups during adsorption [180]. The presence of dissolved organic matter may further enhance NH_4^+ retention through co-adsorption processes [181].

The contribution of BC physical structure remains under debate. NH_4^+ adsorption has frequently been attributed to the combined effects of high SBET, abundant surface functional groups, and physisorption mechanisms [178,180]. Pore-size distribution also influences adsorption because nutrient accessibility differs among macro-, meso-, and micropores. Lyu et al. [182] demonstrated that micropores between 0.6 and 2 nm provide the greatest adsorption capacity, whereas pores smaller than 0.6 nm contribute little to nutrient retention.

Differences in pore architecture generated during pyrolysis further illustrate this behavior. Rice straw-derived BC produced under a CO_2 atmosphere at 600 °C exhibited a micro:meso pore ratio of 43:30:27 and greater NH_4^+ adsorption than BC produced under N_2 or steam atmospheres, whose pore distributions were 26:60:14 and 9:65:26, respectively. Nevertheless, these observations do not fully explain NH_4^+ retention because several studies suggest that surface chemistry exerts a stronger influence than porosity alone [99]. Taken together, the available evidence indicates that efficient NH_4^+ adsorption results from the interaction between pore accessibility and the abundance of reactive surface functional groups rather than from either property acting independently.

Surface oxidation further modifies NH_4^+ adsorption by increasing the abundance of reactive functional groups. Maple wood-derived BC produced at 500 °C for 30 min and oxidized with H_2O_2 exhibited a twofold increase in oxygen-containing functional groups together with a decrease in pH. Although oxidation alone did not immediately increase NH_4^+ adsorption, adjusting the pH to 7 increased adsorption capacity by more than fourfold, indicating that deprotonation of surface functional groups is essential for effective cation exchange [183]. A similar response was observed for Eucalyptus saligna-derived BC produced at 550 °C and oxidized with 5, 10, and 15% (*w/v*) H_2O_2 . Increasing the oxidant concentration progressively enhanced NH_4^+ adsorption after the pH was adjusted to 6.2, further confirming the importance of surface functionality rather than oxidation alone [102].

Feedstock composition also strongly influences NH_4^+ adsorption because it determines the balance between organic functional groups and mineral phases. Co-pyrolyzed BCs produced from sludge and lignocellulosic biomass exhibited adsorption capacities ranging from 0.33 to 2.47 mg $\text{NH}_4^+\text{-N g}^{-1}$, associated with CEC values up to 102.6 cmol⁺ kg^{−1} and the preservation of acidic functional groups at 300 °C [184]. Similarly, apricot shell-derived BC produced at 200–280 °C adsorbed up to 13.5 times more NH_4^+ than other materials while reducing NH_3 volatilization by as much as 37.5% under field conditions, a response attributed to its abundant lactone groups and favorable surface chemistry [185]. These observations indicate that preserving reactive surface groups at relatively low pyrolysis temperatures can be more important than maximizing aromaticity for NH_4^+ retention.

Mineral composition provides an additional adsorption pathway. Woody BCs generally contain lower ash contents than animal-derived BCs but retain mineral phases such as CaO, MgO, Fe_2O_3 , TiO_2 , and Cr_2O_3 , which may contribute to NH_4^+ or NH_3 adsorption and even catalyze ammonium photooxidation [186]. Consistent with this variability, fast-pyrolysis BCs derived from grape skin, pine wood, grape pip, sugarcane pith, maize stover, and rubber tyre exhibited the following adsorption sequence: grape skin > pine wood > grape pip > sugarcane pith > maize stover > rubber tyre. Adsorption was positively correlated with Na, S, and volatile organic matter contents, indicating that feedstock chemistry strongly influences NH_4^+ retention [178].

Pyrolysis temperature modifies these mechanisms but does not produce a universal response. For most plant- and woody-derived BCs with relatively low ash contents, increasing temperature decreases NH_4^+ adsorption because progressive carbonization lowers polarity and reduces the O/C ratio, thereby decreasing the abundance of reactive surface

groups [187]. However, this trend changes in feedstocks rich in minerals. BCs produced from sludge, manure, or co-pyrolyzed mixtures may retain or even increase adsorption capacity because higher ash contents, elevated pH, metal oxides, and greater CEC generate additional retention sites. These contrasting responses indicate that the effect of pyrolysis temperature cannot be interpreted independently of feedstock composition. Instead, NH_4^+ adsorption reflects the balance between the loss of oxygen-containing functional groups and the progressive concentration of mineral phases during thermal treatment.

The variability reported in adsorption experiments supports this interpretation. Yao et al. [101] found that 9 of 13 BCs adsorbed between 1.8 and 15.7% of the NH_4^+ supplied, depending on both feedstock and pyrolysis temperature. Brazilian pepper-derived BC produced at 450 °C exhibited the highest adsorption (15.7%), whereas sugarcane bagasse-derived BC produced at 600 °C showed the lowest value (1.8%). Similarly, Yin et al. [188] reported maximum adsorption capacities of 93.61, 16.95, and 23.07 mg g⁻¹ for sesame straw-derived BC produced at 300, 500, and 700 °C, respectively. The higher adsorption observed at 300 °C was supported by the Freundlich 1/n parameter, indicating greater adsorbent–adsorbate affinity at lower pyrolysis temperatures. Collectively, these findings demonstrate that maximizing NH_4^+ adsorption depends on preserving sufficient surface functionality while maintaining an appropriate pore structure, rather than simply increasing pyrolysis temperature.

Ammonium desorption is generally considered an exothermic and non-spontaneous process that largely reflects the reversibility of cation exchange on BC surfaces [180]. Desorption decreases as pH increases, indicating that stronger electrostatic interactions develop as surface functional groups become progressively deprotonated [180,183]. Conversely, strongly acidic conditions promote NH_4^+ release because positively charged BC surfaces repel the cation, an effect that becomes more evident with increasing agitation time [180]. Complete desorption using KCl solutions further confirms that ion exchange is the dominant retention mechanism for NH_4^+ on BC surfaces. Nevertheless, the extent of desorption varies among feedstocks.

The reversibility of NH_4^+ adsorption remains the subject of discussion. Wang et al. [183] demonstrated, using ¹⁵N-labeled NH_4^+ and poultry litter-derived BC produced at 400 °C, that desorption with water was substantially lower than with KCl. These results confirmed that ion exchange predominates but also showed that adsorption is not completely reversible. The hysteresis observed at pH > 7 was attributed mainly to NH_3 volatilization rather than to irreversible binding with BC functional groups, which accounted for less than 5% of retained NH_4^+ . This interpretation agrees with the findings of Aghoghovwia et al. [178].

Pyrolysis temperature further regulates NH_4^+ desorption by modifying BC surface chemistry. Cai et al. [189] reported that BCs produced from corn cob, pomelo peel, and banana stalk exhibited greater desorption and lower adsorption as pyrolysis temperature increased. Corn cob-derived BC showed the greatest desorption tendency, consistent with the progressive decline in the (O + N)/C ratio caused by thermal carbonization. Similarly, NH_4^+ desorption increased from 41 to 60% as pyrolysis temperature rose from 300 to 800 °C, suggesting that physisorption gradually becomes more important as chemisorption decreases [79,187]. These observations reinforce the conclusion that thermal severity controls not only adsorption capacity but also the reversibility of NH_4^+ retention.

BC aging introduces an additional source of variability. Freshly produced BC generally exhibits limited NH_4^+ adsorption capacity [101]. Progressive oxidation during soil aging increases the abundance of oxygen-containing functional groups, thereby enhancing the potential for cation exchange [190]. However, this response is not universal. In contrast, Wang et al. [183] found that greater oxidation did not increase NH_4^+ adsorption, attributing

this behavior to competition with other exchangeable cations. Similarly, Fe^{3+} and Al^{3+} present in acidic soils may occupy exchange sites and reduce NH_4^+ retention despite increased surface oxidation [100,181]. These contrasting observations indicate that the benefits of oxidation depend on both BC surface chemistry and the ionic composition of the surrounding soil solution.

The influence of BC application rate is equally dependent on soil characteristics. Chicken litter-derived BC exhibited lower NH_4^+ adsorption as the proportion of BC increased in acidic soil [191]. A comparable trend was observed for white wood-derived BC applied to acidic soil, whereas maximum adsorption in alkaline soil occurred at lower BC addition rates [192]. In contrast, *Quercus ilex* L.-derived BC produced at 600 °C increased NH_4^+ adsorption in acidic soil when the application rate increased from 1 to 2% (*w/w*), while no significant response was observed in alkaline soil [147]. These contrasting results indicate that the effect of application rate cannot be generalized because it depends on the interaction between BC properties and soil chemistry.

A similar dependence is observed for NH_4^+ leaching. Ding et al. [193] reported that bamboo-derived BC produced at 600 °C and applied at 0.5% (*w/w*) retained 15.2% of the NH_4^+ present in a sandy-silty soil solution and reduced cumulative NH_4^+ leaching during a 70-day incubation. Dempster et al. [194] found that *Eucalyptus marginata* BC produced at 600 °C reduced NH_4^+ leaching by approximately 20% in sandy soil during the 21 days following fertilization with $(\text{NH}_4)_2\text{SO}_4$. Similarly, peanut hull- and Brazilian pepperwood-derived BCs reduced NH_4^+ leaching by 14.4 and 34.7%, respectively, relative to the untreated control [101]. Collectively, these studies demonstrate that BC consistently reduces NH_4^+ leaching in coarse-textured soils with limited intrinsic retention capacity.

The response becomes more variable as soil texture and mineral composition change. *Pinus radiata* L. BC produced at 450 °C reduced cumulative NH_4^+ leaching by 12, 50, and 86% at application rates of 0.5, 2.5, and 10% (*w/w*), respectively, in acidic sandy soil [195]. By contrast, *Quercus ilex* L. BC produced at 600 °C produced no significant changes in a basic clay loam, where intrinsic NH_4^+ retention was already high, whereas acidic sandy loam initially exhibited increased NH_4^+ concentrations in the leachate before declining after 4–5 weeks, reflecting the progressive development of BC retention capacity [147].

Similarly, higher application rates of maize stover-derived BC reduced NH_4^+ leaching in sandy soil but increased it by 35.6 and 40.3% in sandy loam at application rates of 2 and 4%, respectively. The greater NH_4^+ retention observed in the sandy soil was attributed to enhanced mineralization of organic N induced by higher BC application rates, a trend consistent with the findings of Laird et al. [164]. These contrasting responses demonstrate that the effectiveness of BC for controlling NH_4^+ leaching depends more on soil properties than on BC application alone. Sandy soils generally benefit from greater NH_4^+ retention because of their limited native adsorption capacity, whereas finer-textured soils may show little response or even temporary increases in NH_4^+ mobility depending on pH, mineral composition, BC aging, and the balance between N mineralization and soil retention processes [196].

4.1.4. Nitrate Adsorption and Desorption

Nitrate is highly soluble and is often a dominant mineral N form in well-aerated agricultural soils. In general, most soils have limited capacity to retain NO_3^- because they have low anion exchange capacity at their prevailing pH. Exceptions may occur in some tropical soils rich in Fe and aluminum oxides [117]. BC addition can also reduce bioavailable nitrate indirectly by stimulating microbial N immobilization [8,146]. In addition, some BCs can retain NO_3^- through surface-mediated mechanisms. This process has been described as exothermic in materials rich in lignin, cellulose, and hemicellulose [197].

Nitrate retention by BC is mainly controlled by surface chemistry, pH, and pyrolysis conditions. Hydrogen bonding with basic functional groups has been proposed as one mechanism for NO_3^- retention [137,187,198,199]. However, many BC surfaces are negatively charged because of carboxylic and phenolic groups, which limits NO_3^- adsorption [96]. Under acidic conditions, electrostatic interactions may increase because BC surfaces can become more positively charged [178,200]. Gramüller et al. [201] evaluated NO_3^- adsorption in wood-derived BCs produced between 400 and 900 °C at pH 5 and 7. Adsorption capacities ranged from 700 to 6200 mg NO_3^- -N kg⁻¹ at pH 5, but decreased to 200–2500 mg NO_3^- -N kg⁻¹ at pH 7. The authors attributed this response to the protonation of condensed aromatic structures and to increased anion exchange capacity under acidic conditions. These results show that NO_3^- adsorption is strongly dependent on pH and pyrolysis temperature. The formation of pH-independent oxonium functional groups may also increase anion exchange capacity in BCs [97]. In addition, condensed aromatic rings with reducing character may induce NO_3^- reduction during adsorption experiments. This process can lead to overestimation of the actual adsorption capacity [178,195].

The anion exchange capacity of BC is also affected by biomass and pyrolysis temperature. Although NO_3^- adsorption is generally low, several studies have reported higher retention in BCs produced at higher temperatures [198,202,203].

Sugarcane bagasse, peanut hull, Brazilian pepperwood, and bamboo-derived BCs produced at 600 °C retained 3.7, 2.5, 0.2, and 0.12% of NO_3^- from aqueous solutions, respectively, whereas materials produced at lower temperatures showed no retention capacity [204]. Gai et al. [83] reported that BCs produced at 600–700 °C retained 20–36% more NO_3^- than those produced at 400–500 °C, with rice husk-derived BCs exhibiting the highest adsorption capacity. Similarly, Dempster et al. [194] showed that *Eucalyptus marginata*-derived BC produced at 600 °C adsorbed up to 80% of NO_3^- after 24 h in solution containing 2.5–5 mg NO_3^- L⁻¹. However, this value decreased to 38% when the concentration increased to 50 mg NO_3^- L⁻¹.

In contrast, low-temperature BCs may influence NO_3^- dynamics mainly through microbial immobilization rather than direct adsorption. Gajić and Koch [205] observed that sugar beet-derived BCs produced at 250 °C promoted the immobilization of mineral nitrogen, mainly NH_4^+ and NO_3^- , due to the presence of readily degradable carbon compounds. Other studies have shown that NO_3^- retention varies widely among BCs produced from different feedstocks and pyrolysis systems. In a comparative study, six BCs were evaluated over a concentration range of 5–100 mg NO_3^- L⁻¹: maize stover BC, produced by fast pyrolysis; grape pip BC, grape skin BC, pine wood BC, and rubber tyre BC, obtained by slow pyrolysis; and sugarcane pith BC, produced by vacuum pyrolysis. The adsorption order was rubber tyre BC > grape skin BC > maize stover BC > pine wood BC > grape pip BC > sugarcane pith BC, with rubber tyre BC showing the highest affinity. The authors reported that the distribution coefficient was negatively correlated with pH and positively correlated with Zn content, suggesting that this metal may catalyze NO_3^- reduction in BCs. They also indicated that short equilibrium times may underestimate adsorption capacity [178], consistent with Hollister et al. [203].

Although direct NO_3^- adsorption by BC is usually limited, adsorption–desorption processes can influence NO_3^- transport and residence time in soil. In an alkaline clay soil amended with 5 and 10% sugarcane bagasse-derived BC produced at 800 °C, the maximum NO_3^- concentration in the effluent decreased by approximately 5% after the application of a 20 mg N L⁻¹ KNO_3 solution. The authors concluded that NO_3^- was weakly adsorbed onto BC and could be desorbed under continuous water infiltration. This behavior increased NO_3^- residence time in soil and may increase the probability of plant uptake [198]. Rice husk-derived BC produced at 500 °C and applied at 1 and 3% reduced

NO_3^- leaching by approximately 40% in acidic sandy loam and slightly acidic clay soils, with a stronger effect at the higher dose [206]. Yao et al. [101] observed a 34% reduction in NO_3^- leaching four days after treatment in a sandy soil amended with 2% peanut hull- and Brazilian pepperwood-derived BCs produced at 600 °C. In moderately acidic loam soils, Zea mays-derived BC produced at 350 °C and applied at 5, 10, and 20% reduced NO_3^- leaching under fertilization with 220 kg N ha⁻¹. The strongest reduction, 29%, was recorded at the highest BC dose in the soil with the lowest organic C content [207]. Similar decreases were reported in sandy soils amended with 25 t ha⁻¹ *Eucalyptus marginata*-derived BC produced at 600 °C, where NO_3^- leaching decreased by 25% after 21 days at a fertilization rate of 40 kg N ha⁻¹ [152]. In an acidic sandy soil treated with 0.5, 2.5, and 10% *Pinus radiata* L.-derived BC produced at 450 °C, NO_3^- leaching decreased by 26, 42, and 96%, respectively [195].

However, the effect of BC on NO_3^- leaching is not consistent across soils or application conditions. In a Chinese subtropical soil with pH 4.5, wheat straw-derived BC produced at 600 °C and applied at 40 t ha⁻¹ reduced NO_3^- leaching by 16.15% after 40 h of testing [96]. In an acidic soil fertilized with 170 kg N ha⁻¹, pig manure- and wood-derived BCs produced at 600 °C and applied at 18 t ha⁻¹ reduced NO_3^- leaching by 24 and 26%, respectively, after twelve weeks [208]. Maize stover-derived BC produced at 400–500 °C and applied at 2 and 4% reduced NO_3^- leaching by 29.19 and 28.65%, respectively, in a sandy loam soil with pH 7.30. However, in a sandy soil with pH 7.01, the 4% BC treatment increased NO_3^- leaching by 22.6% compared with the control [196]. In sandy loam (pH 5.65) and clay loam (pH 8.00) soils, *Quercus ilex* L.-derived BC produced at 600 °C and applied at 1 and 2% had only limited effects. Higher NO_3^- losses were recorded at the highest dose compared with unamended soils [147]. These contrasting responses may be associated with soil pH, which regulates surface charge and anion retention. At higher pH, NO_3^- retention tends to decrease, which can favor leaching. Differences among soils with similar characteristics may also reflect BC properties, including pore-size distribution, surface area, volatile matter, and polycyclic aromatic structures with reducing character [151,152]. These properties are controlled by feedstock type and pyrolysis conditions, which can generate contrasting responses even in comparable soils [195,198].

Field-scale evidence also indicates that BC effects on NO_3^- can vary with time and soil depth. Xiao et al. [209] evaluated maize straw-derived BC produced at 400 °C between 2012 and 2014. The amendment did not affect NO_3^- concentration during the first and third years, whereas in the second year it increased NO_3^- concentration down to 20 cm depth. However, when the soil profile was evaluated down to 200 cm, NO_3^- content decreased by 23.3–59.4 kg ha⁻¹, 19.6–70.1 kg ha⁻¹, and 25.8–97.1 kg ha⁻¹ in the first, second, and third years, respectively, compared with the control. These results show that shallow soil measurements may not fully capture the effect of BC on NO_3^- redistribution within the soil profile.

Nitrate desorption depends on the amount previously adsorbed and on pH. Higher pH generally increases NO_3^- desorption from BC [199]. Most studies focused on NO_3^- desorption report low adsorption levels and, consequently, low desorption rates [83,140,179]. In six BCs derived from wheat straw, corn straw, and peanut shell, produced at 400–500 °C for 1.5 h and evaluated at an initial concentration of 50 mg L⁻¹, the desorbed amounts ranged from 0.25 to 0.40 mg NO_3^- g⁻¹, whereas materials produced at higher temperatures (600 and 700 °C for 1.5 h) released lower amounts, ranging from 0.16 to 0.32 mg g⁻¹ [83]. Some studies suggest that NO_3^- can become practically non-desorbable due to changes in the speciation of this readily reducible ion on the BC surface [167,195]. Overall, the contrasting effects of BC on soil N dynamics indicate that nitrate responses are not controlled by a single mechanism. Instead, they result from interactions among BC feed-

stock, pyrolysis temperature, surface chemistry, soil pH, texture, initial N availability, moisture and aeration conditions, and incubation or field-exposure time. These factors determine whether BC mainly promotes N retention, microbial immobilization, mineralization, gaseous losses, or leaching control. To summarize these context-dependent responses, Table 3 presents the main variables and mechanisms explaining divergent nitrogen behavior in BC-amended soils.

Table 3. Key variables and mechanisms controlling divergent nitrogen responses in BC-amended soils.

Nitrogen Response	Divergent Response Patterns	Key Controlling Variables	Main Mechanisms	Reference
N ₂ O emissions	Reduced in some systems but increased or unchanged in others	Feedstock; pyrolysis temperature; initial soil N availability; pH; moisture/aeration; labile C content; incubation time	Regulation of nitrification and denitrification; shifts in redox conditions; enhanced N ₂ O reductase activity; substrate adsorption; electron-transfer processes	[159,173–175,210]
NH ₄ ⁺ retention	Generally increases, although responses vary with feedstock mineralogy and pyrolysis severity	Feedstock; pyrolysis temperature; CEC; ash content; pore structure; pH	Cation exchange; electrostatic attraction; adsorption on oxygen-containing functional groups; mineral-associated retention	[79,178,184,185,187,192,211]
NH ₄ ⁺ leaching	Usually decreases, although responses vary with soil and management conditions	Soil texture; pH; BC dose; fertilizer input; contact time; initial soil N status	Increased NH ₄ ⁺ retention; reduced mobility; adsorption–desorption balance	[147,152,164,193,196]
NO ₃ [−] retention and leaching	Reduced, unchanged, or occasionally increased NO ₃ [−] losses	Soil pH; soil texture; organic C availability; pyrolysis temperature; surface charge; anion exchange capacity	Weak nitrate adsorption; pH-dependent surface protonation; anion exchange; altered water flow and residence time	[117,178,191,199,201,206]
Time-dependent N availability	Initial N immobilization or release may change over time	Incubation time; BC aging; labile C; microbial activity; soil–BC contact time	Mineralization; microbial immobilization; surface oxidation; changes in nutrient retention	[146–148,194]

4.2. Phosphorus

4.2.1. Microbial Phosphorus Transformations

Phosphorus (P) is one of the main limiting nutrients for crop growth. A large fraction of soil P is regulated by precipitation reactions that reduce its availability for plant uptake. In both acidic and alkaline soils, phosphate fertilizer application can promote the formation of poorly soluble secondary compounds, thereby reducing fertilizer-use efficiency [212]. Unlike N, whose availability is strongly governed by microbial transformations, P dynamics are also controlled by geochemical processes across the entire soil pH range [213].

Microorganisms play a central role in regulating soil P availability. Bacteria can immobilize and solubilize inorganic P and mineralize organic P [214]. Fungal communities, particularly arbuscular mycorrhizal fungi (AMF), contribute through a different pathway. They increase root colonization, extend extraradical mycelial networks beyond the root depletion zone, and improve plant access to poorly mobile P forms. Thus, bacteria are mainly involved in P solubilization, mineralization, and microbial immobilization, whereas AMF enhance P acquisition through hyphal exploration and plant–fungus nutrient exchange [215]. Several microorganisms can transform insoluble soil P into HPO₄^{2−}, a form that can be taken up by plants [216,217]. Microbial decomposition of organic matter also

releases organic acids that complex Fe, Al, and Ca cations, reducing P precipitation and increasing P availability [120,218].

BC can influence these processes directly and indirectly. P derived from BC can slowly diffuse into soil and be used by microorganisms and plants [219]. In addition, BC can modify soil physicochemical properties by improving porous structure and increasing surface area, which can favor microbial activity and promote P mineralization and solubilization [220–222]. These effects are not limited to a general stimulation of microbial activity. BC can also selectively enrich functional microbial groups by providing protected pore microhabitats, surface colonization sites, favorable pH and moisture conditions, and nutrient- and carbon-rich microsites that support microbial persistence and activity [215].

Because of these properties, many BCs can act as microbial inoculum carriers [217]. Microorganisms can adhere to BC surfaces and colonize its pores, where they are partly protected from environmental stress and competition. This microenvironment can favor the proliferation of P-solubilizing bacteria, such as *Bacillus* spp., which often face competitive limitations in natural soils [223]. Functional bacterial enrichment may occur through microbial attachment to BC surfaces, pore colonization, extracellular polymeric substance-mediated adhesion, and nutrient retention within BC microsites [215]. This bacterial enrichment may occur through microbial attachment to BC surfaces, pore colonization, extracellular polymeric substance-mediated adhesion, and nutrient retention within mechanisms can improve microbial survival, functional persistence, and the potential for P dissolution. Consistent with this role, several studies have reported increased phosphatase activity in BC-amended soils [15,222]. Field evidence has also shown that BC application can increase available P, plant P accumulation, cottonseed yield, and phosphate fertilizer-use efficiency under different P fertilization rates [15].

Biochar-based microbial inoculation has also shown positive effects on P release. He et al. [69], evaluated rice husk-derived BC inoculated with two P-solubilizing bacteria, *Lysinibacillus sphaericus* and *Lysinibacillus fusiformis*. In leaching assays, inoculated BC increased P concentrations in the leachates compared with the non-inoculated BC. Phosphate increased by 54 and 47%, and orthophosphate increased by 57 and 43%, respectively. The authors attributed these increases to the release of organic acids within the BC microenvironment, which transformed insoluble P into soluble forms. These results are consistent with previous findings [224].

Changes in microbial ecology have also been reported in BC-amended soils. In a pot experiment using a silty loam soil, *Pinus radiata*-derived BC promoted the proliferation of phosphate-solubilizing bacteria and potentially reduced bacterial plant pathogens [225]. In P-limited soil planted with *Lolium perenne*, *Miscanthus giganteus*-derived BC produced at 600 °C for 15 min increased the abundance of P-mobilizing bacteria. These included rhizospheric microorganisms involved in aromatic sulfonate desulfurization, phosphonate mobilization, phosphate ester mobilization, and tricalcium phosphate solubilization [226]. These responses may be related to BC-induced changes in soil pH. Since many P-solubilizing bacteria show greater activity at pH values between 6 and 8, BC-induced shifts toward near-neutral conditions may favor their development. In this study, phosphonate-utilizing bacteria increased by up to 24 and 12% in the treatments with 1 and 2% BC, respectively. In contrast, tricalcium phosphate-solubilizing bacteria decreased from 17% in the control soil to 4 and 14% in the 1 and 2% BC treatments, respectively [226]. These results show that BC does not uniformly stimulate all P-mobilizing microbial groups. Instead, it can selectively favor specific functional groups depending on soil conditions and P form.

These findings are consistent with broader evidence showing increases in P availability after BC application. DeLuca et al. [116] and Zheng et al. [227] reported increases in P availability of up to 10- and 100-fold, respectively, in BC-amended soils compared

with control soils. Recent evidence also indicates that BC can interact with AMF to promote P uptake through both fungal and bacterial pathways. In maize, the combined application of BC and AMF increased mycorrhizal colonization, biomass, and P uptake, particularly under P-deficient conditions [215]. This interaction was associated with the enrichment of phosphate-solubilizing microorganisms, including *Streptomyces*, *Bacillus*, *Pseudomonas*, *Bradyrhizobium*, *Arthrobacter*, and *Micromonospora*. It was also associated with higher abundance of P-cycling genes involved in inorganic P solubilization and organic P mineralization, including *gcd*, *phoD*, and *ugpQ*. These findings suggest that AMF can recruit P-solubilizing microorganisms through mycelial exudates and carbon-rich compounds, while BC provides porous microhabitats and nutrient-retention sites that facilitate microbial colonization and functional activity [215].

The effect of BC on microbial P cycling also depends on the initial availability of soil P. In low-P rice-cropping soil, maize straw-derived BC produced at 500 °C for 2 h promoted the growth of phosphate-solubilizing bacteria such as *Bacillus*, *Pseudomonas*, and *Rhizobium*. Their abundances increased by 66.6, 21.8, and 65.2%, respectively [228,229]. However, positive microbial responses are not always accompanied by increased enzymatic activity. Some studies have reported lower activity of P-solubilizing enzymes after BC application, which has been attributed to increased electrical conductivity at potentially inhibitory levels and to possible enzyme denaturation. Overall, BC can enhance microbially mediated P availability by acting as a P source, modifying soil pH, providing microbial habitats, supporting inoculant survival, and promoting functional microbial groups involved in P solubilization and mineralization. However, these effects are context-dependent. Differences among studies may be associated with BC feedstock, pyrolysis conditions, soil pH, electrical conductivity, initial P status, microbial community composition, and evaluation time. This temporal factor is particularly important because studies range from days to years, while BC weathering, microbial colonization, and interactions between solubilized P and organic or inorganic soil compounds evolve over time [124].

4.2.2. Phosphorus Bioavailability

The addition of BC may represent an alternative strategy to improve P availability in soil [119]. Several authors have reported increases in extractable phosphate in soils amended with different carbonaceous materials [7,140,230]. These increases are often associated with changes in soil P fractions rather than with a direct P contribution from BC itself. However, neutral effects or even reductions in bioavailable P have also been reported [122]. Therefore, the effect of BC on P availability should be interpreted as context-dependent rather than universally positive.

BC can modify P bioavailability through several mechanisms. First, it can increase soil pH and reduce Al^{3+} and Fe^{3+} activity [21,212,213]. However, BC may also increase the presence of Ca^{2+} and Mg^{2+} , which can precipitate P under specific conditions [212]. Second, BC can promote microbial activity and organic P mineralization [21,214]. Third, P bound to organic molecules through ester or pyrophosphate bonds (P-O-P) can be released during carbonization as soluble or exchangeable P salts [136,231]. Fourth, BC can protect soluble P from adsorption onto Al and Fe oxides, such as gibbsite ($\text{Al}(\text{OH})_3$) and goethite ($\alpha\text{-FeOOH}$), because BC anion-exchange sites may compete with mineral adsorption sites [216]. Associated dissolved organic matter may also reduce Fe^{3+} to Fe^{2+} , favoring P release from minerals. Finally, BC can increase soil ion exchange capacity and retain phosphate ions through electrostatic attraction, hydrogen bonding, or complexation with divalent ions [102,200,204,217–219]. Together, these interactions favor P transfer into the soil solution and improve plant uptake and accumulation [225].

P insolubilization is strongly controlled by pH because this parameter regulates the speciation of Al, Fe, Ca, and Mg. In alkaline soils, P solubility is mainly controlled by its interaction with Ca. This interaction can lead to the formation of poorly soluble calcium phosphate phases, including apatite-group compounds, $(\text{Ca}_5(\text{PO}_4)_3, (\text{F}, \text{Cl}, \text{OH}))$ [122,136,232]. In acidic soils, P availability is mainly limited by Al^{3+} , Fe^{2+} , and Fe^{3+} , which can form Al and Fe phosphates with very low solubility. In BC-based P fertilizers, phosphate phases associated with Ca and Mg can also regulate P release. Ca-enriched BCs may limit P availability through the formation of low-solubility Ca-phosphate phases, whereas Mg-enriched BCs can favor more soluble phosphate forms and greater P release [232]. Thus, BC can influence P precipitation by modifying pH and ionic strength [122], or by adsorbing metal cations involved in P fixation [116,212]. BC surfaces can also adsorb polar and non-polar organic molecules, including organic acids, phenolic acids, amino acids, proteins, and complex carbohydrates. This interaction may limit the formation of chelates between these compounds and metal cations [212].

The effect of BC on soil P availability is closely related to feedstock type and pyrolysis conditions. In general, fresh biomasses contain higher concentrations of soluble P than their corresponding pyrolyzed materials. Among BCs, animal waste-derived materials usually contain the highest P percentages (Table S2) [96,221]. Marchetti and Castelli [222] and Inal et al. [125] showed that manure-derived BCs can supply more plant-available P than inorganic phosphate fertilizers. In these materials, total P content tends to increase as pyrolysis temperature rises from 650 to 700 °C [223,233]. Raw manure contains P mainly as orthophosphate, pyrophosphate, and monoesters. During pyrolysis, these species are transformed into inorganic P forms with different solubility and bioavailability [224,233]. Therefore, the relative abundance of Ca and Mg-associated phosphate compounds controls the kinetics of P release from manure-derived BCs [232,233].

Although higher pyrolysis temperatures can increase total P content, they can also reduce P extractability [33]. In pig manure-derived BC produced at 400 and 700 °C P was released more rapidly from the material produced at 400 °C during the first 40 h. Release profiles differed throughout the 300 h assay. In the BC produced at 700 °C, P release increased over time but remained very low, ranging from 0.004 to 0.0158 g kg⁻¹. In contrast, the BC produced at 400 °C released more P, reaching 0.33 g kg⁻¹. The authors attributed this behavior to the formation of $\text{Ca}_3(\text{PO}_4)_2$ and the reduction of $\text{Na}_4\text{P}_2\text{O}_7$ at higher pyrolysis temperature [233]. This evidence indicates that total P concentration alone is not sufficient to predict the agronomic value of BC. The chemical form of P and its release kinetics are equally important.

Feedstock P content also determines the amount and form of available P in BC. Zhang et al. [226] evaluated nine BCs derived from different materials: *Eucalyptus pilularis* wildfire residues produced at 350–500 °C; sugarcane bagasse produced at 350 °C for 1 h; peanut shell, green waste, and *Imperata cylindrica* produced at 450 °C for 1 h; and *Eucalyptus marginata*, *Eucalyptus polybractea*, *Pinus radiata*, and softwood mixtures produced at 720 °C for 20 min. All materials contained available P, but the amounts differed markedly. *Imperata cylindrica*-derived BC showed the highest extractable P content, exceeding 700 µg P g⁻¹. In contrast, BCs derived from *Eucalyptus pilularis* wildfire residues, *Eucalyptus marginata*, *Pinus radiata*, and softwood mixtures showed the lowest extractable P concentrations, below 200 µg P g⁻¹. Overall, BC can increase, maintain, or reduce P bioavailability depending on the interaction among soil pH, metal cation activity, feedstock composition, pyrolysis temperature, P speciation, and release kinetics. This explains why BCs with high total P contents do not always provide the highest amount of plant-available P. To synthesize these feedstock- and pyrolysis-dependent responses, Table 4 summarizes the main trends affecting P availability in BC-amended soils.

Table 4. Feedstock- and pyrolysis-dependent trends affecting phosphorus availability in BCs.

Factor	Condition	Implications for P Availability	Key Explanation	Reference
Feedstock	Plant-derived BCs	Generally lower nutrient-source potential	Lower total P content and variable P speciation	[136,226,231,232]
Feedstock	Animal-derived BCs	Generally higher nutrient-source potential	Greater total P content and abundance of Ca- and Mg-associated phosphates	[117,125,224,233]
Pyrolysis temperature	Low (<500 °C)	Higher short-term P release	Greater proportion of labile and extractable P forms	[33,232,233]
Pyrolysis temperature	High (>600 °C)	Lower immediate P release despite higher total P	Formation of more stable phosphate minerals	[33,233]

4.2.3. Phosphorus Adsorption and Desorption

Phosphorus adsorption by BCs is controlled by multiple mechanisms and may vary according to BC modification, surface chemistry, and solution conditions. In several studies, P adsorption has been described as endothermic and non-spontaneous [180,200,234]. In a Mg-enriched tomato leaf-derived BC produced at 600 °C, P adsorption followed relatively slow kinetics that fitted a third-order model ($n = 1.74$; $R^2 = 1.00$), suggesting that more than one mechanism contributed to phosphate retention [228].

Phosphate adsorption is commonly described using Langmuir and Freundlich isotherms. In many cases, the Langmuir model provides the best fit [7,99,229,234]. However, model performance can differ among BCs. Yao et al. [228] reported that most evaluated models adequately described phosphate adsorption, except the Freundlich model. In that study, the best fits were obtained with the Langmuir–Freundlich and Redlich–Peterson models, indicating heterogeneous adsorption behavior. The maximum phosphate adsorption capacity of the Mg-modified tomato tissue-derived BC produced at 600 °C, was 116.58 mg g^{−1}. Similarly, Ya et al. [235] reported a maximum adsorption capacity of 109.35 mg g^{−1} for a Mg-modified bamboo-derived BC produced at 600 °C. This process fitted the Langmuir model ($R^2 = 0.988$) and pseudo-second-order kinetics ($R^2 = 0.990$) and was described as spontaneous and endothermic. The dominant mechanism involved MgHPO₄ formation through electrostatic attraction and surface precipitation. Liang et al. [236] showed that Mg- and Fe-modified rice straw-derived BC reached a maximum adsorption capacity of 6.93 mg P g^{−1} at 25 °C. This value was higher than those obtained for BCs modified only with Mg (5.75 mg P g^{−1}) or Fe (0.23 mg P g^{−1}). At 350 °C, the capacity increased to 8.13 mg P g^{−1}, confirming a favorable endothermic process. Spectroscopic analyses indicated that retention occurred mainly through chemisorption and precipitation of Mg and Fe phosphates.

Several surface mechanisms can explain phosphate adsorption by BCs. A significant fraction of P can bind through anion exchange with oxonium groups and protonated aromatic structures. Phosphate can also be retained through electrostatic attraction in the presence of cations such as K⁺ and NH₄⁺, or through cation bridging mediated by divalent cations between phosphate and negatively charged hydroxyl or carboxyl groups on the BC surface [99,199,204,217,237]. In modified BCs, phosphate may also be adsorbed onto Mg oxide nanoparticles. Hydrogen bonding can occur between dihydrogen phosphate and hydroxyl, carboxyl, carbonyl, or undissociated phenolic groups [217], as well as with dissolved organic matter located within the micropores of oxidized BCs [102]. However, aging may reduce phosphate adsorption capacity because of the loss of oxonium groups and progressive oxidation of organic compounds [111]. The stability of these interactions depends

strongly on solution pH [235,237]. further indicated that surface charge and precipitation reactions may be more important than surface area in controlling phosphate adsorption.

The adsorption and desorption of P in carbonaceous materials depend on biomass type, pyrolysis conditions, surface area, functional groups, and phosphate concentration in solution [7,164,219,234]. Some studies show lower adsorption capacity at higher pyrolysis temperatures. For BCs produced from three biomasses, materials obtained at 600 °C showed adsorption capacities 4 to 10-fold lower than those produced at 400 and 500 °C. The distribution coefficients at 400 °C were 51.3, 19.8, and 10.5 L kg⁻¹, whereas at 600 °C they decreased to 1.1, 2.0, and 0.9 L kg⁻¹ for BCs derived from Embaúba (*Cecropia hololeuca* Miq.), Lacre (*Vismia guianensis* Aubl. Pers.), and Ingá (*Inga edulis* Mart.), respectively [238]. In contrast, other studies indicate that higher carbonization severity can increase phosphate adsorption [229]. This increase may result from precipitation reactions with Ca and Mg derived from BC, whose concentrations tend to increase with pyrolysis temperature.

Mineral-enriched BCs can show high phosphate adsorption through precipitation mechanisms. Yu Liang et al. [200] reported that a BC composed of phosphogypsum and rapeseed straw pyrolyzed at 700 °C reached a maximum adsorption capacity of 102.25 mg g⁻¹ according to the Langmuir model. This material achieved complete phosphate removal from solution at pH 8. Kinetic data fitted the pseudo-second-order model, and spectroscopic analyses indicated that the dominant mechanism was the precipitation of Ca₅(PO₄)₃OH like compounds. Similarly, a tobacco stem-derived BC produced by direct pyrolysis at 800 °C for 1 h under N₂, with in situ incorporation of Ca and Mg, increased the maximum soil P adsorption capacity from 0.77 mg g⁻¹ in control to 1.18 mg g⁻¹ with 3% BC. The process fitted the Langmuir model (R² > 0.90) and the pseudo-second-order kinetic model (R² up to 0.97), indicating a predominant chemisorption favored by Ca²⁺ and Mg²⁺ on the BC surface.

Feedstock type can also explain large differences in phosphate adsorption. Zhang et al. [226] evaluated nine BCs and observed that *Eucalyptus pilularis* wildfire-derived BC (350–500 °C), sugarcane bagasse-derived BC (350 °C, 1 h), green waste- and blade grass-derived BCs (*Imperata cylindrica*; 450 °C, 1 h), and *Eucalyptus marginata*-derived BC (720 °C, 20 min) did not adsorb P. In contrast, *Pinus radiata*-derived BC, softwood mixture-derived BCs (720 °C, 20 min), and peanut shell-derived BC (450 °C, 1 h) adsorbed between 1 and 2% of P from a 200 mg P L⁻¹ solution. *Eucalyptus polybractea*-derived BC produced at 720 °C showed the highest adsorption capacity, with P retention values of 5.24 and 2.19% in solutions containing 100 and 200 mg P L⁻¹, respectively. Yao et al. [101] found no clear relationship between carbonization temperature and P adsorption in BCs derived from sugarcane bagasse, peanut hull, Brazilian pepperwood, and bamboo. These contrasting results show that pyrolysis temperature alone does not explain phosphate adsorption capacity.

High P adsorption capacity has been reported for several BCs. However, in soil–BC systems, P adsorption can decrease depending on pH and BC dose. As pH increases, soil and BC surfaces become more negatively charged, which favors electrostatic repulsion of phosphate anions and reduces P adsorption [191,217]. Phosphate concentration can also modulate the effect of BC on soil adsorption capacity. In an acidic sandy clay loam soil amended with 7.4, 13.8, and 19.4% chicken litter-derived BC, P adsorption decreased as BC dose increased at low P concentrations. However, from 1250 µg mL⁻¹ onward, P concentration in the equilibrium solution remained almost constant [191]. Very limited P adsorption has also been reported in rice husk-derived BCs. This behavior was attributed to the absence of Mg salts and to the high initial P content of the material. The small fraction adsorbed at high P concentrations was associated with the low pH of the solutions, which increased the positive surface charge of BC [239,240].

Evidence from soil assays further shows that BC can either reduce or increase P adsorption depending on soil properties. In a tropical acidic soil from Colombia with high P retention capacity, the addition of *Eucalyptus globulus*-derived BC decreased P fixation as the BC proportion increased. Maximum adsorption values declined from 1513.75 to 540.27 mg kg⁻¹ as BC addition increased from 0 to 35% [241]. A similar response has been observed for other BCs applied to acidic soils [242]. In contrast, an experiment with three soils of different acidity showed that increasing BC dose increased P adsorption in the acidic soil but slightly decreased it in the alkaline soil. The increase in P adsorption was attributed mainly to BC-derived Ca, which can act as a bridge between P and BC or promote P precipitation. The precipitation of Fe and Al oxides or phosphates after BC-induced pH increases was considered less important [212].

Soil–BC contact time also affects P adsorption. Morales et al. [238] reported that, after 240 days of incubation, the P adsorption capacity of a soil with an initial pH of 4.1 decreased. In another study 0, 15, and 30 t ha⁻¹ of a BC produced from a mixture of *Picea abies* (L.) H. Karst. and *Pinus sylvestris* L. at 550–600 °C were applied to one sandy soil (pH 5.9) and two clay soils (pH 5.4 and 6.2), no increase in P adsorption capacity was observed in any of the evaluated soils [242]. These results indicate that short-term and long-term responses may differ, and that soil–BC contact time should be considered when interpreting phosphate adsorption.

Phosphate desorption from BCs depends on feedstock, pyrolysis conditions, phosphate concentration, coexisting ions, and soil type. Corn cob-derived BC and fig-tree pruning wood-derived BC, both produced at 600 °C for 10 h, desorbed 70 and 76% of the initially adsorbed P, respectively [243]. Increasing pyrolysis temperature may also increase P desorption. Gong et al. [79] observed that, in rice straw-derived BCs produced between 300 and 800 °C, higher carbonization temperature gradually increased the proportion of physical adsorption relative to chemical adsorption. Since physically adsorbed P is more easily released, this shift favored desorption. In a comparative study using three BCs obtained under slow and fast pyrolysis conditions, Ingá-derived BC (*Inga edulis* Mart.) produced by slow pyrolysis adsorbed less P but retained larger amounts than Embaúba-derived BC (*Cecropia hololeuca* Miq.) and Lacre-derived BC (*Vismia guianensis* Aubl. Pers.). This result suggests that Ingá-derived BC could improve P retention in sandy soils with low adsorption capacity [238].

Desorption also depends on the initial P content of BC and the concentration range evaluated. Assays conducted with 25 to 400 mg P dm⁻³ and BCs derived from sugarcane bagasse and *Miscanthus giganteus* produced at 300–700 °C for 20 or 60 min showed similar percentages of desorbed P for both feedstocks, with maximum desorption reaching 46% at the highest concentration [234]. Soluble P originally present in BC can also contribute to P release. For example, a cocoa shell-derived BC containing 3990 ± 138 mg kg⁻¹ of P, 37% whereas in a corn cob-derived BC containing 697 ± 23 mg kg⁻¹ of P, desorption reached 25% [244]. Consistently, soil-column leaching assays conducted at pH 6.2 with 4% rice husk-derived BC, which had a high initial P content of 8.6 g kg⁻¹ showed cumulative P release 72% higher than that of the control soil [245]. Conversely, in soil-column assays at pH 4.8, the addition of 2% pecan shell-derived BC produced at 700 °C for 1 h and containing 263 mg kg⁻¹ of P increased P retention and reduced P levels in leachates by 60 and 65% after 25 and 67 days of incubation, respectively [246].

In soil–BC systems, P release is controlled by the interaction among BC dose, soil type, initial P concentration, and extraction conditions. In wheat straw-derived BCs produced at 350–550 °C, both the amount and percentage of desorbed P were influenced by initial P concentration, BC application rate, and soil type. In alkaline soils, higher BC addition was associated with greater P bioavailability. In acidic soils, higher BC application increased

P availability only at low nutrient concentrations, when evaluated over 0–240 mg P L^{−1} using a solid ratio of 1:10 [212]. Martínez et al. [7] evaluated *Eucalyptus globulus*-derived BC produced at 450 °C for 3 h in an acidic soil over a concentration range up to 1000 mg P kg^{−1}, also using a solid ratio of 1:10. After eight consecutive extractions, cumulative desorbed P increased with the initial P concentration. These findings show that P behavior in soil–BC systems reflect a dynamic balance among release, precipitation, adsorption, and desorption processes. The direction and magnitude of this balance depend on BC properties, soil characteristics, and environmental conditions [200].

Unlike N, phosphorus behavior in BC-amended soils is mainly governed by the balance among solubilization, adsorption, precipitation, desorption, and release. This balance is highly sensitive to soil pH, feedstock mineral composition, pyrolysis conditions, initial P status, BC dose, and soil–BC contact time. To clarify these context-dependent patterns, Table 5 summarizes the main factors that regulate P availability, retention, and release in BC-amended soils.

Table 5. Context-dependent controls on phosphorus availability, retention, and release in BC amended soils.

P-Related Process	Divergent Response Patterns	Key Controlling Variables	Main Mechanisms	Reference
P bioavailability and plant uptake	P availability and plant uptake may increase, remain unchanged, or decrease depending on soil and BC properties	Soil pH; initial soil P; feedstock P content; Ca, Mg, Fe, and Al availability; pyrolysis temperature; BC dose	pH-mediated changes in P solubility; release of soluble P; organic P mineralization; precipitation of Ca-, Mg-, Fe-, or Al-phosphate phases	[21,115,122, 212,231,232, 247]
Microbial P solubilization and mineralization	Microbial P mobilization is often stimulated but may be limited under unfavorable soil conditions	BC porosity; surface area; soil pH; available C; microbial community structure	Microbial colonization; organic acid release; phosphatase activity; mineralization and solubilization of P compounds	[21,217,232, 248–250]
Phosphate adsorption capacity of BCs	Phosphate adsorption may increase or decrease depending on BC mineral composition and production conditions	Feedstock; pyrolysis temperature; Ca, Mg, Fe, and Al content; surface functional groups; phosphate concentration	Anion exchange; ligand exchange; cation bridging; surface complexation; precipitation of phosphate minerals	[200,234–236,239,251]
Soil P adsorption and retention	Soil P retention may increase or decrease after BC application	Soil pH; soil texture; intrinsic P retention capacity; BC dose; Ca availability; contact time	Competition with Fe/Al oxides; surface-charge modification; Ca-mediated precipitation; changes in P sorption sites	[7,212,242]
P desorption, release, and leaching	P release may increase nutrient availability or contribute to losses under some conditions	Feedstock; pyrolysis temperature; initial P content; phosphate concentration; soil type; competing ions	Desorption processes; dissolution of phosphate minerals; concentration-gradient effects; soil-controlled P mobility	[79,201,235, 243]
Time-dependent P behavior	Short- and long-term P responses may differ as BC ages	Incubation time; BC aging; oxidation; soil–BC contact time; organic matter interactions	Surface oxidation; microbial modification of P cycling; shifts among release, adsorption, and precipitation processes	[102,111,239, 245]

4.3. Potassium

4.3.1. Microbial Potassium Transformations

Potassium (K) is an essential macronutrient involved in key physiological processes that regulate crop growth, yield, and quality. In soil, microorganisms contribute to K dynamics mainly by promoting mineral weathering and the release of non-exchangeable K into the soil solution. This differs from N and P, whose microbial transformations involve multiple redox, mineralization, or immobilization pathways. Therefore, microbially

mediated K availability is primarily associated with solubilization processes rather than with direct transformation among multiple chemical species [252].

Soil microorganisms, through their involvement in physical and chemical processes, constitute a determining factor in K dynamics; consequently, changes in bacterial community structure can significantly affect its availability. In contrast to N and P, where microbial transformations involve multiple redox or mineralization pathways, microbially mediated K availability is mainly associated with mineral weathering and the release of non-exchangeable K into the soil solution. Bacteria such as *Bacillus mucilaginosus*, *Bacillus edaphicus*, *Acidithiobacillus ferrooxidans*, *Paenibacillus* spp. and *Bacillus circulans* have been identified in soil as being capable of directly solubilizing K from minerals, releasing it into the soil solution [253]. Their solubilizing capacity is associated with the secretion of organic acids, which promote mineral dissolution and may complex mineral-associated ions, including silicon, thereby favoring the release of K into more available forms [254,255]. The survival and activity of K-solubilizing bacteria depend on soil pH, water content, nutrient availability, the nature of K-bearing minerals, and climatic conditions [256]. The effect of these strains has been reported to be greater on illite than on feldspars, since illite provides a more favorable habitat for microbial population development [257].

The application of BCs to soils, such as Entisols and Alfisols, has been shown to promote the abundance of K-solubilizing bacteria [258]. Therefore, BC may influence K dynamics not only through its intrinsic mineral composition, but also indirectly by improving microbial habitats, modifying soil physicochemical conditions, and stimulating K-solubilizing bacterial activity. The addition of maize stover-derived BC at 0.6% to soil increased the activity of *Bacillus mucilaginosus* by 80%, a value five times higher than that observed in the control, while also generally improving soil conditions. Consequently, K mobilization increased from 12.3 to 46.0%, which was attributed to the stimulation of microbial activity in the presence of BC [259]. These findings suggest that the effect of BC on K availability is strongly mediated by the interaction between BC-induced changes in soil conditions and the functional activity of K-solubilizing bacterial groups, rather than by a purely chemical release process alone.

4.3.2. Potassium Bioavailability

Potassium (K) may originate from either organic or mineral sources [117]. Although total K content in soil is often high, only a small fraction is available for plant uptake because most K is associated with soil minerals and is not readily accessible [258,260]. Soil K is commonly distributed among four main fractions: water-soluble K, exchangeable K, non-exchangeable K, and structural or mineral K [261,262]. Water-soluble and exchangeable K are the most available forms for plants. Non-exchangeable K is also referred to as slowly available K, whereas structural K is generally poorly available [117].

Soluble K represents the immediately available fraction, although it usually accounts for only a small proportion of total soil K. Exchangeable K is the most widely used indicator for assessing soil K nutritional status and estimating fertilization requirements [263]. Non-exchangeable K is mainly located between the tetrahedral layers of tri- and dioctahedral micas, vermiculites, and interstratified minerals. In arid and semi-arid soils, more than 90% of total K may occur within the structure of primary minerals, such as muscovite, biotite, and feldspars. This fraction is slowly released through weathering processes. These K pools are dynamically connected. When soluble and exchangeable K decrease, non-exchangeable K can be released into the exchangeable phase to re-establish equilibrium. Conversely, after K fertilizer application, K fixation may occur in some minerals, depending on soil mineralogy and fixation capacity. Therefore, the release rate of K from non-exchangeable

fractions largely determines soil K fertility status. Root K uptake can also be limited by competition with other cations in the soil solution, which affects K-use efficiency [263].

BC can increase available K in soil through direct and indirect mechanisms [264–266]. Directly, BC can supply K contained in its ash and soluble mineral fractions. Indirectly, it can promote transformations among soil K fractions and favor the release of non-exchangeable K into more available forms [263]. BCs have been reported to retain K during pyrolysis, although the amount retained depends on production temperature [114,267]. K concentrations in BCs can range from 0.70 to 116 g kg^{−1} [123]. Unlike C and N, K volatilizes mainly at relatively high temperatures, usually above 700 °C [116]. This favors K enrichment in BCs produced below this threshold.

In BCs, K generally occurs in soluble forms, such as KCl, K₂SO₄, KNO₃, and KNO₂, which can represent 50–58% of total K [268]. However, K can also occur in less soluble forms. For example, in straw-derived BC produced at 400 °C, the insoluble K fraction was identified as complex K compounds intercalated between the layers of a more ordered graphite-like carbonaceous structure [39,259]. These forms are relatively stable in soil and can dissolve gradually during BC aging [269]. In pine- and grass-derived BCs containing 15–20% oxygen and produced at 625 °C, K was associated with oxygen-containing functional groups, such as phenoxides. At temperatures above 300 °C, K present in BC can also be incorporated into silicate structures. These findings indicate that BC-derived K availability depends not only on total K content, but also on the chemical form and structural location of K within the material.

Table S2 shows that the BCs with the highest K content correspond to poultry litter produced at 400 °C, with values of 7.01% [125] and 5.59% [51], rice straw produced at 500 °C, with 4.80% [88], and maize straw produced at 600 °C, with 4.57% [212]. In contrast, the BCs with the lowest K contents were bagasse produced at 600 °C, with 0.15% [270], Douglas fir wood produced at 500 °C, with 0.15% [271], pine woodchips produced at 450 °C, with 0.17% [272], and rice husk produced at 300 °C, with 0.18% [119]. Overall, Table 2 suggests that total K content tends to increase with pyrolysis temperature up to 600 °C, although this trend is not universal, as shown by bagasse-derived BC [212]. This variability confirms that feedstock type remains a primary control on BC K content.

Poultry-litter BCs have been shown to increase soil pH, extractable inorganic N, exchangeable K, and available P, thereby enhancing plant growth. However, high application rates may induce Ca-Mg nutritional imbalances in plant tissues [273]. A banana peel-derived BC produced at 400 °C showed a particularly high K content of 42.55% [274]. In BCs obtained from 14 tropical plant residues, total K content ranged from 0.35 to 5.1%, whereas water-soluble K, which represents the readily available fraction, ranged from 0.04 to 3.0% [275]. Similarly, extractable K content in BCs varies according to biomass type and pyrolysis conditions [269,276]. These results show that high total K content does not always correspond to high readily available K, because soluble, exchangeable, and structurally bound K fractions differ among BCs.

In sewage sludge-derived BCs with initial K contents of 14%, available K decreased by less than 1% during pyrolysis. In addition, increasing the production temperature from 250 to 600 °C doubled total K concentration from 0.5 to 1.1% [277]. In giant reed-derived BCs produced between 300 and 600 °C, extractable K increased with increasing pyrolysis temperature [78]. A similar trend was observed in rice straw-derived BC produced for 1 h between 300 and 400 °C. However, above 500 °C, extractable K decreased [278]. In a study by Zolfi-Bavariani et al. [51], poultry manure-derived BCs produced at 200, 300, and 400 °C for 4 h and applied to a calcareous soil significantly increased K availability when the BC produced at 400 °C was used, compared with materials obtained at lower

temperatures [164]. These contrasting results indicate that pyrolysis temperature can increase total or extractable K only within specific feedstock-dependent ranges.

K bioavailability in soil increases after BC application [264,279,280], especially when BCs are produced from K-rich crop residues, such as wheat and maize straw [281]. In an alkaline sandy soil with pH 8.26, palm- and guava branch-derived BCs applied at 2.4 and 4.8 Mg ha⁻¹ showed contrasting effects on K availability. Palm-derived BC, which had higher total K content (4.54%) and higher CEC (37.9 cmol⁺ kg⁻¹), significantly increased exchangeable K, especially at the 4.8 Mg ha⁻¹. In contrast, guava-derived BC, with lower K content (0.29%) and lower CEC (17.6 cmol⁺ kg⁻¹), did not significantly increase exchangeable K [280]. This comparison shows that the effect of BC on K availability depends on both its K content and its capacity to retain and exchange cations [276].

Several mechanisms explain the increase in soil K availability after BC addition. These include the presence of basic cations that do not volatilize during pyrolysis [263,281], the release of water-soluble and exchangeable K fractions from BC, and the alkalizing effect of BC, which increases the density of negative charges on soil particles [282]. However, K release from BC may be limited by its association with insoluble salts, the physical inaccessibility of K to water, microbial processes, and pore-size constraints. In addition, greater K release from K-bearing minerals after the application of organic sources may increase the risk of leaching in coarse-textured soils. This highlights the need to evaluate nutrient supply, retention, and loss processes simultaneously. In soil studies using BCs derived from hardwood waste products, pine chips, and poultry litter produced at 500 °C, materials containing water-soluble salts, such as KNO₃, KCl and Ca₃(PO₄)₂, favored K⁺ from BC [283]. By contrast, lignocellulosic BCs showed minimal K release, which was attributed to their low K contents and to the probable association of K with structural forms that are not accessible to water [284].

Pot experiments also confirm the strong effect of BC type and dose on available K. In two soils, Ultisol and Alfisol, tobacco straw-derived BC produced at 400 °C for 3 h and applied at 0, 1, 2, 4, and 10% increased available K by 109.07–1789.70%. This response was associated with an increase in soil pH from acidic values of approximately 5–6 to near-neutral values of approximately 6–7.5 [227]. Similarly, corn cob-derived BC applied to a calcareous sandy soil significantly increased soluble and available K across all BC-soil ratios, even at low application rates. Soluble K increased from 100.4 to 232.7 mg kg⁻¹, and available K increased from 421.3 to 740.6 mg kg⁻¹ after the application of 60 mg ha⁻¹ of BC [264]. Bamboo-derived BC produced at 450 °C with a pH of 9.5 also increased K availability by 13.6–40.5% in an Entisol [255]. These effects have also been observed under deficit irrigation. Under these conditions, wheat straw-derived BC significantly increased available soil K by 17.54–88.45% and plant K content by 3.84–14.41%, improving biomass production and harvest index [282].

Soil mineralogy is another important factor controlling K availability after BC addition. Studies have shown that the mineralogical composition of soil clays strongly influences K content, transformation, and availability [282,285]. Therefore, BC-induced changes in the clay fraction may alter soil K dynamics. In a nine-year field study conducted in a brown soil with pH 5.65, continuous application of corn straw-derived BC produced at 450 °C and applied at 1500–6000 kg ha⁻¹ increased available K by 17.21–51.98% and slowly available K by 31.73–54.01%. These changes were associated with increased illite content and higher K concentrations at surface, edge, and interlayer adsorption sites [279]. Consistently, short-term experiments demonstrated that K release from BC corresponds to a rapid chemical process mediated by organic acids, in which carboxyl groups act as hydrogen donors that displace K into the soil solution [286].

Overall, BC can improve K bioavailability through direct K supply, release of soluble and exchangeable K, alkalization-induced changes in soil charge, stimulation of K release from non-exchangeable pools, and modification of clay-associated K dynamics. However, these effects depend strongly on feedstock type, pyrolysis temperature, BC mineral composition, soil texture, clay mineralogy, application rate, and soil moisture conditions. Therefore, BCs with high total K content should not automatically be interpreted as highly efficient K sources. Their agronomic value depends on the proportion of readily available K, the stability of insoluble K forms, the risk of leaching, and the capacity of the soil–BC system to retain and gradually supply K to plants. To synthesize these patterns, Table 6 summarizes the general trends in K content and availability as affected by feedstock type and pyrolysis temperature.

Table 6. General trends in potassium content and availability as affected by feedstock type and pyrolysis temperature.

Factor	Condition	Main Trend	Reference
Feedstock	Plant-derived BCs	Highly variable K content; crop residues often show high K concentrations	[263,281]
Feedstock	Animal-derived BCs	Can substantially increase exchangeable K in soil	[51,125,287]
Pyrolysis temperature	Increasing temperature (up to ~600 °C)	Generally increases K concentration in BCs	[51,78,212]
Pyrolysis temperature	>700 °C	May reduce K retention because of volatilization	[116,267]

4.3.3. Potassium Adsorption and Desorption

The number of studies on K adsorption is lower than that conducted for N and P, and they mainly focus on BC-soil systems. The incorporation of BCs into soil can increase K retention capacity [165]. This occurs because positively charged ions such as K^+ can be adsorbed onto negatively charged surfaces, including carboxyl and phenolic functional groups present in both soil minerals and BCs [288]. In addition, the high specific surface area of BC can provide extra adsorption sites for K. This may allow larger nutrient reserves to be maintained in amended soils compared with soils without BC application [227,269].

K adsorption behavior varies according to BC type, soil properties, and the experimental system. Some studies have reported that the Freundlich model describes K adsorption better than the Langmuir model. In a study using white wood-derived BC produced at 450–500 °C and applied to sandy and silty loam soils, K adsorption data fitted the Freundlich model more closely. The results showed that K adsorption capacity decreased at higher K application rates. In the silty loam soil with low CEC, K adsorption capacity decreased significantly after BC addition, which was attributed to competition from other cations present in the material [192]. In contrast, chicken litter-derived BC showed a different response. Increasing the BC dose increased K adsorption, and the material showed high affinity for ionic K forms. However, in aqueous K solutions prepared at different concentrations, the data fitted the Langmuir model more closely. K release was also observed, which was attributed to the initial K content of the BC [191]. These contrasting results indicate that BC can act both as a K adsorbent and as a K source, depending on its composition and the surrounding matrix.

BC may increase K leaching when it supplies large amounts of mobile K. At the same time, it can increase soil CEC and strengthen nutrient retention. Therefore, its effect on K losses depends on the balance between K release and K retention. In a column experiment with rice grown in two soil types, sandy soil with pH 7.0 and clay soil with pH 6.8, rice husk- and rice straw-derived BCs produced at 400–450 °C increased K concentrations

in the leachate by 292% in the sandy soil compared with the control. In contrast, BC application had no significant effect on K leaching in the clay soil [289]. This difference suggests that soluble K, soil texture, BC composition, and nutrient interactions jointly regulate K mobility [269]. In acidic jointly regulate K mobility clay soil columns amended with poultry litter-derived BC produced from an 80:20 pine chip/poultry litter mixture, K release showed a rapid initial phase followed by a marked decrease in dissolved K in the leachate [269]. This pattern suggests that part of the BC-derived K is rapidly released, whereas another fraction may be retained or gradually depleted over time.

Post-production chemical modification can strongly alter K adsorption–desorption behavior. Mahdi Najafi-ghiri et al. [290] showed that an alkaline spent coffee grounds-derived BC increased K release up to 1383 mg kg^{-1} , compared with 908 mg kg^{-1} in the control soil with pH 8.37, after the addition of 500 mg kg^{-1} K. In contrast, acidified BC reduced K release to 979 mg kg^{-1} , showing that chemical modification can decrease the progressive supply of K. Successive CaCl_2 extractions confirmed that alkaline BC favored the gradual release of K in calcareous soils. Similar results were reported in a calcareous soil amended with BCs derived from urban waste and coffee residues, as well as their acidified forms. Coffee-derived BC showed the highest total K content, $15,700 \text{ mg kg}^{-1}$, whereas acidification reduced this value to 2160 mg kg^{-1} . This treatment decreased the soluble K fraction but favored a higher proportion of K retained in exchangeable forms. In successive CaCl_2 extractions, coffee-derived BC released up to 1383 mg kg^{-1} of K, whereas the acidified material released 979 mg kg^{-1} . The combination with bentonite increased the Ca/K ratio to 5.55, suggesting greater cation retention and a shift in the competitive balance between K^+ and Ca^{2+} in the exchange complex [263]. These findings show that K release depends not only on the initial K content of BC, but also on chemical modification, cation competition, and interactions with other soil amendments.

Consistent with these findings, Ayman [280] reported that BC application at 3% *w/w*, produced at 450°C for 4 h, significantly modified the thermodynamic parameters of K adsorption–desorption in different Egyptian soils. In sandy soil, labile K increased from 0.055 to $0.112 \text{ cmol}^+ \text{ kg}^{-1}$, corresponding to a 103.6% increase, with maize stover residue-derived BC. In calcareous soil, labile K increased from 0.043 to $0.408 \text{ cmol}^+ \text{ kg}^{-1}$, corresponding to an 849% increase. The potential buffering capacity of K increased up to $61.779 \text{ cmol}^+ \text{ kg}^{-1} (\text{mol L}^{-1})^{-0.5}$, and Gibbs free energy (ΔG) reached more negative values, up to $-4.833 \text{ kcal mol}^{-1}$. These changes indicate more thermodynamically favorable K exchange processes after BC application. K adsorption–desorption dynamics in BC–soil systems are controlled by the dual role of BC as both a K source and a K-retaining material. These dynamics depend on biomass type, pyrolysis temperature, initial K content, soluble salt composition, soil texture, CEC, competing cations, and post-production chemical modifications. Therefore, increased K release after BC application should not automatically be interpreted as improved K-use efficiency. It may also increase the risk of K mobility in coarse-textured soils. Conversely, BCs that retain a larger fraction of K in exchangeable forms may improve the buffering capacity of the soil–BC system and support a more gradual nutrient supply.

4.4. Sulfur

4.4.1. Microbial Sulfur Transformations

Sulfur (S) is essential for plant growth, detoxification, defense, and stress resistance. It is involved in protein synthesis, is a component of sulfolipids in photosynthetic membranes, and indirectly affects nutrient-use efficiency. Most soil S originates from parent geological material. However, approximately 95% of soil S occurs in organic forms, mainly as sulfate

esters and sulfonates [291]. These forms are not directly available to plants and must be converted into inorganic forms through microbial processes.

Microbial communities regulate S availability through two main pathways. Heterotrophic bacteria and fungi are mainly involved in the mineralization of organic S compounds. In contrast, sulfur-oxidizing bacteria contribute to the oxidation of reduced S forms toward sulfate [292,293]. This distinction is important for BC-amended soils because S availability depends on both enzymatic organic S mineralization and microbial oxidation. Numerous soil bacteria and fungi can hydrolyze sulfate ester bonds, releasing plant-available S. Long-term evidence from agricultural soils further indicates that S speciation is strongly controlled by soil organic carbon and pH. Organic amendments can increase reduced C-bonded S forms and may therefore influence S availability in cropping systems [294].

Some studies in BC-amended soils have reported increased organic S mineralization [295,296]. This response should not be attributed only to direct S release from BC. It may also result from BC-induced changes in soil temperature, pH, aeration, microbial habitat quality, and substrate availability. BC can darken the soil surface, which may promote faster warming and increase the rates of S mineralization or oxidation [296]. It can also supply trace elements at relatively high concentrations. This may stimulate autotrophic microorganisms such as *Thiobacillus*, which are among the most relevant bacteria involved in S oxidation in soils [297].

The chemical form of S in BC is also relevant for microbial transformations. C-S bonds represent an important substrate for S mineralization [295,298]. Their presence in BC may therefore favor this process after soil application. In soil-BC incubation studies, a decrease in C-S bonds were observed after three days of incubation. This suggests an intensification of the initial phase of macronutrient mineralization [299]. Under anaerobic conditions, organic S mineralization involves the progressive oxidation of C-S bonds into more oxygenated species, such as sulfoxides and sulfones. These compounds can act as intermediates in the final conversion to sulfate [298].

Pyrolysis conditions strongly influence S speciation in BC. As pyrolysis temperature increases, organic S is progressively transformed into inorganic S. In oak- and corn stover-derived BCs, S was identified mainly as sulfate at 500 and 600 °C [291]. Similar results were reported by Wang et al. [300] in straw-derived BCs produced at 900 °C and by Knudsen et al. [301] in wheat straw-derived BCs produced at 1100 °C. These findings indicate that high-temperature BCs tend to contain S in more stable inorganic forms, whereas low-temperature BCs may preserve a larger proportion of organic S. This temperature-dependent transformation has important implications for S availability. BCs produced at lower temperatures may provide more organic S substrates for microbial mineralization after soil incorporation. In contrast, BCs produced at higher temperatures may contain more inorganic sulfate-like forms, which may be more stable but less dependent on microbial mineralization. Therefore, the microbial contribution to S availability after BC application is closely linked to the S form inherited from the feedstock and modified during pyrolysis. It also depends on the capacity of soil microbial communities to mineralize organic S and oxidize reduced S compounds.

Taken together, these findings show that BC can influence soil S dynamics through both biological and chemical pathways. Its effect is not limited to the direct input of S. It also depends on how BC modifies soil temperature, pH, aeration, microbial habitat conditions, trace-element supply, and the chemical speciation of S. This explains why the contribution of BC to S availability may differ among feedstocks, pyrolysis temperatures, soil redox conditions, and microbial communities.

4.4.2. Sulfur Bioavailability

The content and speciation of S in BCs depend on both feedstock type and pyrolysis conditions. In corn straw-derived BC, 40–50% of total S was present as sulfate, whereas 50–60% occurred as protein-associated S. During pyrolysis at 400 °C, 35–50% of total S was released in gaseous form. At temperatures between 500 and 700 °C, S speciation changed markedly. Sulfate decreased from 21.1 to 3.1%, respectively, which was attributed to its conversion into insoluble sulfides, such as CaS and K₂S, within the BC matrix [302].

Some studies indicate that S content decreases as pyrolysis temperature increases, mainly because of S volatilization as organic compounds [25,114]. In *Pennisetum purpureum*-derived BC, S content remained relatively stable at low temperatures [303]. However, S availability decreased when pyrolysis temperature increased from 400 to 600 °C [304]. A similar trend was observed in coconut fiber-derived BCs, where S content decreased from 0.34% at 350 °C to 0.19% at 600 °C, suggesting a low S contribution from this type of agricultural biomass [305]. Likewise, in maize straw-derived BC, S content decreased from 0.58% at 300 °C to 0.46% at 500 °C and 0.32% at 700 °C [306].

The pyrolysis atmosphere can also influence S transformation. In urban sludge with relatively high S content (0.62%), pyrolysis relatively high S content (0.62%), pyrolysis under a CO₂ atmosphere between 300 and 700 °C favored the decomposition of S-containing species. Emissions of SO₂ and H₂S increased as temperature increased [307]. However, this temperature-dependent decline in S retention is not universal. Devi and Saroha [308] reported that S content in BCs derived from paper-industry effluent treatment plant sludge increased from 0.35 to 0.40% as pyrolysis temperature increased from 300 to 700 °C, with an atypically high value of 0.977% at 500 °C. A similar increasing trend was reported for pig manure-derived BCs [309]. These contrasting responses suggest that S retention during pyrolysis is controlled not only by temperature, but also by feedstock mineral composition, ash content, and the chemical forms of S present in the original biomass.

The trends summarized in Table 2 further show that S content differs strongly among biomass types. The highest S contents were reported for date palm-derived BC produced at 300 °C, with 2.14% [65], *Conocarpus*-derived BC produced at 200 °C, with 2.28% [114] and sewage sludge, with 1.01% [127]. In contrast, the lowest S contents were reported for maize-derived BC, with 0.37%, and soybean stover-derived BC, with 0.40% [123]. In general, the highest S contents in Table 2 correspond to woody residues, whereas the lowest values are associated with agricultural biomasses. For most biomasses included in Table S2, total S content decreases as pyrolysis temperature increases. An exception is pig manure-derived BC, in which S content increased from 0.24 to 0.39% as temperature rose from 400 to 600 °C [309].

BC addition to soil can increase S bioavailability, but the response depends on dose and soil conditions. In a 100-day incubation study using a strongly acidic Acrisol (pH 3.8), forage radish seed cake-derived BC increased available S by 1.25 and 5.5 mg L^{−1} at low application rates of 5 and 10 g L^{−1}, respectively. However, doses above 15 g L^{−1} showed diminishing returns, and the highest dose of 40 g L^{−1} did not differ significantly from the control. In another study, the application of 2% corn stover-derived BC to a soil reported as calcareous with pH 4.4 increased inorganic S and total S contents in soil. It also promoted significant S accumulation in plant leaves and roots [299].

4.4.3. Sulfur Adsorption and Desorption

The number of studies on S adsorption by BCs is limited. The available evidence suggests that S release and retention are controlled by pyrolysis temperature, extractant type, solution pH, and the interaction between sulfate and reactive BC surface sites. In dairy manure-derived BCs produced at different pyrolysis temperatures, pot experiments with a

calcareous soil were used to evaluate S extracted with H₂O, NaH₂PO₄, and HCl solutions. In water extracts, extractable sulfate decreased as pyrolysis temperature increased from 300 to 700 °C. In contrast, HCl and NaH₂PO₄ extracts showed the opposite trend [306]. This indicates that increasing pyrolysis temperature may reduce the readily soluble sulfate fraction, while increasing the fraction associated with more strongly retained or less water-extractable S forms. The authors reported that the pseudo-second-order kinetic model provided the best fit to the experimental data ($R^2 > 0.8$). This suggests that the rate-limiting step in sulfate release may involve chemical interactions between S and the BC surface, together with the decomposition of organosulfur compounds. The sulfate release rate decreased over time and depended on both pyrolysis temperature and initial concentration. Greater SO₄^{2−} release was observed in BCs produced at higher temperatures, with reported values of 0.85, 2.30, and 5.53 g mg^{−1} h^{−1} at 300, 500, and 700 °C, respectively [306].

A subsequent study using dairy manure-derived BC produced at 700 °C for 6 h confirmed the importance of surface-mediated sulfate retention. In this material, SO₄^{2−} adsorption kinetics also followed a pseudo-second-order model ($R^2 = 0.943$), while both Freundlich and Langmuir models adequately described the adsorption isotherms. Solution pH was a key factor controlling SO₄^{2−}. The amount adsorbed progressively decreased as pH increased from 2 to 12 [251]. This behavior was attributed mainly to electrostatic interactions. At low pH, BC surfaces contain more positively charged sites that can retain sulfate. As pH increases, these sites decrease and competition with hydroxyl ions becomes stronger, reducing SO₄^{2−} adsorption [310].

Similar behavior was reported by Kang et al. [311] in pig manure-derived BCs. The authors found that S adsorption onto BC produced at 700 °C was spontaneous, supporting the role of high-temperature manure-derived BCs as materials capable of retaining sulfate under favorable surface-charge conditions. However, the evidence also indicates that sulfate retention is strongly pH-dependent and may be limited under alkaline conditions. These findings suggest that BC does not act only as a source of S, but also as a material capable of regulating sulfate release and retention. High pyrolysis temperatures may reduce water-extractable sulfate while increasing more strongly bound S fractions. At the same time, sulfate adsorption depends strongly on pH because electrostatic attraction decreases as BC surfaces become less positively charged. Therefore, the contribution of BC to S availability in soil depends on the balance between soluble sulfate release, organosulfur decomposition, sulfate adsorption, and pH-controlled desorption.

4.5. Calcium

4.5.1. Microbial Calcium Transformations

Calcium (Ca) is a key structural and functional element in soil–plant systems. It plays an important role in plant physiology and soil geochemical dynamics. Ca represents approximately 3.64% of the Earth's crust [312] and is the third most abundant macronutrient in plants after nitrogen and potassium. In plant tissues, Ca²⁺ contributes to cell wall stability, membrane integrity, and calcium-dependent intracellular signaling [313]. In soil, it contributes to aggregate stabilization, organomineral complex formation, and the regulation of soil organic carbon [314,315]. However, the distribution of Ca among soil fractions is not static. It is strongly influenced by microbial processes that regulate Ca precipitation, fractionation, mobilization, and recycling. In BC-amended soils, these processes may be further affected by BC-induced changes in pH, alkalinity, porosity, microbial habitat conditions, and ash-derived Ca inputs, especially in mineral-rich or high-ash BCs.

The most widely documented microbial mechanism involved in Ca transformation is microbially induced calcium carbonate precipitation (MICP), as described by Song et al. [316] and Kim et al. [317]. In this process, microorganisms convert soluble

Ca^{2+} into solid CaCO_3 , mainly calcite, through the generation of CO_3^{2-} under alkaline conditions. The predominant pathway is ureolysis, in which urea hydrolysis increases pH and promotes carbonate precipitation. Other pathways, including oxalotrophy and the degradation of nitrogenous compounds, may also contribute to CaCO_3 formation [317]. This mechanism differs from K or P solubilization processes. In the case of Ca, microbial transformation often involves immobilization or redistribution into secondary carbonate phases rather than a simple increase in dissolved Ca availability. In experimental systems, an oxalotrophic strain belonging to the family Comamonadaceae removed up to 85% of dissolved Ca, demonstrating high immobilization efficiency.

Microorganisms can also induce the formation of vaterite. Its nucleation occurs within bacterial biofilms, where the extracellular matrix provides reactive sites that favor local supersaturation [317]. Several bacterial families can induce MICP, including Bacillaceae, Pseudomonadaceae, Moraxellaceae, Xanthomonadaceae, and Comamonadaceae [317]. Among them, *Sporosarcina pasteurii* is widely recognized for its high urease activity and efficiency in biomineralization applications [316]. These findings indicate that bacterial communities are the main microbial drivers of Ca biomineralization, mainly through ureolysis, biofilm-mediated nucleation, and carbonate precipitation.

Calcium is not only transformed by microorganisms. It can also regulate microbial community structure. Dou et al. [314] showed that, in soils with high CaCO_3 contents of up to 143.82 g kg^{-1} , the relative abundance of Proteobacteria and Chloroflexi increased, whereas Acidobacteria decreased. A general tendency toward lower overall bacterial diversity was also observed. This ecological effect is closely linked to organic carbon accumulation, because Ca contributes to organomineral complex formation and aggregate stabilization [315]. In calcareous soils, exchangeable Ca and organic-bound Ca can represent important proportions of total Ca, reaching 20.06–57.86% and 26.69–73.91%, respectively [315]. These values suggest that Ca–microbiota interactions can influence soil organic carbon mineralization and stabilization.

In BC-amended systems, these interactions may become more complex. BC can indirectly affect Ca-associated microbial processes by modifying soil pH, aggregation, and microbial habitats. It can also provide reactive surfaces for organomineral associations and create microsites where CaCO_3 precipitation and Ca-organic matter interactions may occur. Therefore, the role of BC should not be interpreted only as the direct release of ash-derived Ca. Its effect may also involve changes in the local conditions that regulate microbial carbonate precipitation, Ca redistribution, and Ca-mediated stabilization of organic matter.

The available evidence shows that microbial Ca transformations in soil involve three main processes: immobilization through alkalinity-driven precipitation, structural reorganization into organomineral complexes, and ecological regulation of bacterial communities according to CaCO_3 availability. The reported removal of up to 85% of dissolved Ca [317], the high proportions of exchangeable and organic-bound Ca in calcareous soils [315], and the effect of CaCO_3 on bacterial community structure [314] confirm that Ca is a biologically regulated element. For BC-amended soils, Ca dynamics should therefore be interpreted as the result of interactions among BC mineral composition, soil alkalinity, microbial carbonate precipitation, and Ca-mediated stabilization of organic matter. This interpretation is more appropriate than considering Ca behavior as a purely chemical nutrient-release process.

4.5.2. Calcium Bioavailability

Calcium (Ca) in soil occurs in primary minerals, such as feldspars and amphiboles, and in secondary minerals, including calcite (CaCO_3) and dolomite [$\text{CaMg}(\text{CO}_3)_2$]. These secondary phases are particularly abundant in calcareous soils [318]. In addition to these

relatively stable mineral forms, Ca is also present in exchangeable fractions adsorbed onto mineral colloids and in fractions associated with organic matter. These pools represent the most dynamic Ca reservoir in soil. Ca availability depends on parent material, degree of weathering, leaching, and soil pH. These factors regulate the equilibrium between structural Ca forms and fractions that are potentially accessible to plants.

In soil-BC systems, Ca^{2+} bioavailability is determined by chemical fractionation, incorporation into the exchange complex, and persistence in plant- and microbially accessible forms. Therefore, total Ca concentration alone is not sufficient to predict Ca availability. Bioavailable Ca is mainly associated with exchangeable fractions and organic matter-bound forms, which contribute to plant nutrition and soil structural stability. In calcareous soils, Dou et al. [315] showed that exchangeable Ca represents 20.06–57.86% of total Ca, whereas Ca bound to organic fractions represents 26.69–73.91%. These values indicate that a substantial proportion of soil Ca can occur in potentially available or functionally active forms. The same study showed that increasing CaCO_3 content from 4.29 to 143.82 g kg^{-1} modified bacterial community structure and promoted soil organic carbon stabilization. This directly links Ca availability with aggregation and carbon protection processes [315].

BC incorporation can significantly modify the exchangeable Ca reservoir in agricultural soils. Ma and Matsunaka [319] reported soil Ca concentrations of 760 mg kg^{-1} in a soil with pH 4.61 after the application of dairy cattle manure-derived BC produced at 450 °C for 4 h. This indicates substantial Ca release into the exchangeable phase. Under field conditions, wood-derived BC applied at 0.8–20 t ha^{-1} increased bioavailable Ca by 101–320% over four years [320]. This suggests a persistent effect on the exchange complex. Similar responses have been reported in Ferrosols and Calcarosols amended with paper industry residue-derived BC produced at 550 °C, where Ca concentrations reached 8.87 and 20.3 $\text{cmol}^+ \text{kg}^{-1}$, respectively [172]. In greenhouse assays, Uzoma et al. [321] observed an increase in exchangeable Ca from 0.24 to 0.29 g kg^{-1} after the application of cattle manure-derived BC produced at 500 °C. This increase was accompanied by greater Ca uptake in maize and was attributed to the positive relationship among total soil carbon, Ca, and cation exchange capacity.

However, Ca bioavailability can be reduced under acid deposition. Liu et al. [322] documented a decrease in surface Ca from 0.47 to 0.36% between 1995 and 2010, with annual losses of 0.026 g kg^{-1} soil. This result highlights the vulnerability of exchangeable Ca to H^+ -induced leaching and displacement by Al^{3+} . In this context, Jing et al. [313] emphasized the need to increase base saturation through Ca-rich amendments to mitigate Al toxicity and restore root functionality in acidic soils. This evidence supports the use of Ca-bearing amendments, including mineral-rich BCs, in systems where Ca depletion and acidity limit root performance.

The potential of BC as a Ca source is strongly controlled by its initial mineral content, which varies widely with feedstock type and pyrolysis temperature. Animal waste-derived BCs generally contain much higher Ca concentrations than lignocellulosic BCs. For example, turkey litter-derived BC contains 4.04 and 5.61% Ca at 350 and 500 °C, respectively [25]. Poultry litter-derived BC can reach 4.54% at 500 °C [323], while chicken manure-derived BC increases from 1.98% at 250 °C to 3.03% at 550 °C [324]. Swine manure-derived BC reached 2.89% at 600 °C [110]. In contrast, agricultural and woody biomasses usually show lower values, including barley straw with 0.20% [325], macadamia shell with 0.37% [326], sugar maple sawdust with 0.50% [327], and *Acacia* with 0.27% [328]. This difference is substantial. A turkey litter-derived BC containing 5.61% Ca may contain approximately 28 times more Ca than a barley straw-derived BC containing 0.20%.

Some BCs show exceptionally high Ca concentrations. These include *Conocarpus*-derived BC produced at 800 °C, with 67.50% Ca [114], goat manure-derived BC with 9.3%

Ca at 600 °C [273], and urban wastes-derived BC with 8.1% at 600 °C [89]. In contrast, Douglas fir wood-derived BC produced at 500 °C contained only 0.20% [271] and bamboo-derived BC with 0.22% at 300 °C [212]. These differences confirm that feedstock type is a primary determinant of Ca content in BC. In most materials, Ca content increases with pyrolysis temperature because mineral ash becomes progressively concentrated. For example, poultry litter-derived BC increased from 2.66% Ca at 350 °C to 4.54% at 500 °C [25]. However, this trend is not universal. Oak wood-derived BC decreased from 2.70% Ca at 400 °C to 0.31% at 600 °C [89], and date palm-derived BC decreased from 2.14% at 300 °C to 0.54% at 800 °C [65]. These exceptions show that mineral enrichment during pyrolysis depends on the specific mineral composition and thermal behavior of each biomass. This demonstrates that mineral dynamics depend on the specific composition of the biomass.

These patterns indicate that BCs with high Ca contents can improve Ca bioavailability, especially when Ca is present in exchangeable or reactive mineral forms. However, high total Ca concentration should not automatically be interpreted as high agronomic effectiveness. The availability of Ca after BC application depends on its chemical form, solubility, interaction with the soil exchange complex, soil pH, leaching conditions, and competition with other cations. Therefore, animal waste-, sludge-, and some urban waste-derived BCs may be more relevant as Ca sources than woody or low-ash lignocellulosic BCs, but their effectiveness must be evaluated in relation to soil acidity, base saturation, and plant demand. Beyond the direct mineral contribution of raw BCs, modified BCs can also influence nutrient retention processes. Mg-modified BCs have been proposed as nutrient-retaining amendments capable of enhancing NH_4^+ and PO_4^{3-} adsorption through struvite formation and Mg-P precipitation, while also contributing to N_2O mitigation. Although this mechanism is more directly related to Mg- and P-mediated nutrient retention than to Ca supply, it illustrates how mineral modification of BC can alter nutrient availability and retention pathways in soil–BC systems.

4.5.3. Calcium Adsorption and Desorption

Unlike Ca bioavailability at the soil-system scale, Ca^{2+} adsorption and desorption by BC occur mainly as interfacial processes. These processes are controlled by pore structure, functional group density, and mineral phases formed during pyrolysis. Together, these properties determine surface retention, binding strength, and the reversibility of Ca^{2+} release. Eraliev et al. [329] showed that pyrolysis at 800 °C of a mixture of mussel shells and spent coffee grounds produced a composite BC enriched in CaO through thermal decarbonation. The material had a specific surface area of $37.8 \text{ m}^2 \text{ g}^{-1}$ and a mean pore diameter of 37.7 nm. Ca^{2+} adsorption followed the Langmuir model, indicating monolayer adsorption on relatively homogeneous sites. The maximum adsorption capacity reached of 375.6 mg g^{-1} . The adsorption kinetics fitted a pseudo-second-order model, suggesting that chemisorption was the dominant process. This behavior was associated with chemical interactions between Ca^{2+} and carboxylic or phenolic groups.

A different mechanism was reported by Jajarmi et al. [330]. In that study, bagasse-derived BC adsorbed Ca^{2+} from CaCl_2 solutions up to 0.6 mol L^{-1} mainly through electrostatic interactions. This process was related to cation exchange between Ca^{2+} and negatively charged functional groups, such as deprotonated carboxyl and phenolic groups. In this case, adsorbed Ca^{2+} reduced soil water repellency by modifying surface free energy, without necessarily requiring the formation of reactive Ca oxides. This comparison shows that Ca^{2+} retention by BC can occur through different pathways depending on the mineral composition of the material and the degree of thermal transformation.

Pyrolysis temperature is therefore a key factor controlling the Ca^{2+} adsorption–desorption equilibrium. At high temperatures, around 800 °C, mineralization and CaO

formation may dominate. This favors strong chemisorption and lower reversibility [329]. In contrast, BCs produced at intermediate temperatures, around 400–500 °C, may preserve more oxygen-containing functional groups. These groups can increase CEC and favor more reversible cation-exchange processes. This behavior is consistent with evidence showing that BC can retain cationic nutrients such as NH_4^+ through exchange-related mechanisms, although retention depends on ionic form and application rate [164].

Desorption occurs when competing cations or changes in solution chemistry alter the surface equilibrium. Under low-pH conditions, Al^{3+} can displace Ca^{2+} through cation exchange [313]. Acid deposition can also promote surface protonation, which favors Ca^{2+} release from active sites [322]. The intensity of this process depends on the density of active sites, the chemical form of retained Ca, and the degree of carbonization of the BC. In summary, high-temperature BCs maximize specific adsorption capacity, reaching up to 375.6 mg g^{-1} , through the formation of reactive mineral phases, whereas intermediate-temperature BCs favor greater reversibility and control during desorption. These findings indicate that high-temperature BCs can maximize Ca^{2+} adsorption capacity through the formation of reactive mineral phases, as shown by adsorption values up to 375.6 mg g^{-1} [329]. However, stronger retention may reduce reversibility and limit controlled Ca^{2+} release. In contrast, intermediate-temperature BCs may offer lower adsorption capacity but greater exchangeability, making Ca^{2+} release more responsive to soil chemical conditions. Therefore, the selection of pyrolysis conditions should be aligned with the intended function of the BC. High-temperature, Ca-rich BCs may be more suitable when strong Ca^{2+} retention or immobilization is desired, whereas intermediate-temperature BCs may be more appropriate when gradual release and exchangeable Ca supply are the main objectives.

4.6. Magnesium

4.6.1. Microbial Magnesium Transformations

Magnesium (Mg^{2+}) is an essential macronutrient for plants, animals, and humans. Its deficiency can reduce productivity and quality in both agricultural and forest systems [331–333]. In plants, Mg^{2+} is the central atom of the chlorophyll molecule and plays a key role in photosynthesis, carbohydrate metabolism, enzyme activation, and nucleic acid synthesis [334,335]. It also participates in photosynthetic CO_2 fixation [336,337], defense against abiotic stress [338], and central metabolic pathways such as glycolysis and the tricarboxylic acid cycle [117]. Because Mg^{2+} is highly mobile in the phloem, it can be redistributed toward growing organs, where it supports vegetative and reproductive development [339,340].

In soil, Mg is mainly distributed among primary and secondary mineral fractions, exchangeable fractions, and soluble fractions. Exchangeable and soluble Mg are the most directly available forms for plant uptake [336,341]. Soil Mg dynamics are closely linked to biological processes that regulate Mg release, redistribution, and persistence in labile pools. These processes are particularly important in acidic soils, where Mg deficiency is common [342]. In BC-amended soils, Mg dynamics may also be influenced by changes in pH, cation exchange capacity, porosity, microbial habitat conditions, and the contribution of ash-derived Mg-bearing phases, especially in mineral-rich BCs.

Microbially mediated Mg transformations differ from those of redox-active nutrients. Mg does not undergo microbial oxidation or reduction. Instead, its biological regulation occurs mainly through mineralization, solubilization, and biogeochemical mobilization. These processes control the redistribution of Mg among mineral, soluble, and exchangeable fractions. Therefore, unlike N and S, Mg cycling does not involve microbial redox pathways, but rather biologically mediated release, recycling, and cation-exchange processes.

Mineralization represents the release of Mg structurally incorporated into plant residues and microbial biomass after decomposition. Although organic Mg accounts for less than 1% of total soil Mg [336], the decomposition of plant tissues and microbial biomass provides a continuous flux of Mg into the soil solution. Once released, Mg can be reincorporated into the exchangeable fraction [252]. This pathway is important because it represents an internal biological recycling mechanism within the soil–plant–microorganism system.

Solubilization involves the release of Mg from primary and secondary Mg-bearing minerals through microbial modification of the rhizosphere. In highly weathered acidic soils, exchangeable Mg^{2+} is often low, while H^+ and Al^{3+} dominate the exchange complex [342]. Under these conditions, microorganisms can locally modify pH and rhizosphere chemistry through metabolites produced during organic matter decomposition. These metabolites include organic acids and other low-molecular-weight compounds that can promote mineral weathering and favor the transfer of Mg from mineral-associated forms into the soil solution [252]. Although Mg is not redox-active, its release from minerals is strongly conditioned by these microbially induced chemical changes.

Biogeochemical mobilization refers to the movement and redistribution of Mg^{2+} after its release into the soil solution or exchange complex. Microbial activity can indirectly modify Mg dynamics by influencing pH, proton concentration, and cation competition in the rhizosphere. These factors regulate the equilibrium between soluble and exchangeable Mg [336]. In acidic soils, competition with H^+ and Al^{3+} limits the persistence of Mg at exchange sites [342]. Microbial changes in the rhizosphere may therefore favor the temporary reincorporation of Mg into labile pools or promote its movement to deeper soil layers through changes in cationic equilibrium. Because BC can increase soil pH and provide additional exchange surfaces, its interaction with microbial activity may help regulate the balance among Mg solubilization, exchangeable Mg retention, and potential leaching losses in acidic soils.

The relationship between exchangeable Mg and the microbiota is also reflected in changes in microbial community structure and function. In acidic soils with different levels of Mg deficiency, exchangeable Mg and pH explained more than 50% of the variation in bacterial composition, while electrical conductivity was also identified as a significant factor. Differences in the relative abundance of several bacterial genera were observed between soils with low and moderate Mg deficiency [343]. This evidence shows that Mg availability is not controlled only by abiotic soil chemistry. It also interacts with bacterial community structure, especially in acidic environments where pH and exchangeable cation dynamics are closely coupled.

From a functional perspective, Mg also contributes to bacterial metabolic pathways. These include carbon metabolism, amino acid biosynthesis, the citrate cycle, carbon fixation in prokaryotes, and pyruvate metabolism. In the evaluated deficiency levels, the relative contribution of Mg to these pathways exceeded 40% [343]. These results indicate that Mg availability is linked not only to soil chemical pools, but also to microbial metabolic functionality, particularly in energy-related and carbon-assimilation processes.

Mg^{2+} also performs essential structural and catalytic functions in microbial cells. It acts as a cofactor in enzymes involved in central metabolism and contributes to the stabilization of ribosomes and nucleic acids [344]. Therefore, the microbial cycle of Mg should be understood as a process of recycling, release, and redistribution. Although it does not involve redox transformations, it plays an important role in the biological regulation of Mg availability in acidic soils [342].

For BC-amended systems, Mg dynamics should be interpreted as the result of interactions among BC mineral composition, pH regulation, exchange-site availability, microbial decomposition, and rhizosphere-driven mineral solubilization. This interpretation is more

appropriate than considering Mg behavior as a purely chemical release process. BC may influence Mg availability not only by supplying ash-derived Mg, but also by modifying the soil conditions that regulate microbial activity, cation exchange, and Mg redistribution within the soil profile.

4.6.2. Magnesium Bioavailability

Magnesium (Mg) bioavailability in soil is determined by its distribution among chemical fractions, its interaction with the exchange complex, and the physicochemical conditions that regulate its persistence in the soil solution. These components operate together and define the fraction of Mg that is potentially available for root uptake.

The distribution of Mg among chemical fractions determines the size of the immediately available pool. Soil Mg occurs as water-soluble Mg, exchangeable Mg, Mg associated with weakly retained or carbonate-bound fractions, organically complexed Mg, and structural or mineral Mg [345]. Structural or mineral Mg is usually the dominant fraction in most soils. Although total Mg content may be high, the exchangeable fraction represents approximately 5% of total Mg. Together with soluble Mg, this fraction constitutes the compartment most directly accessible for root uptake. The organic matter-associated fraction represents less than 1% of total Mg because Mg^{2+} has low affinity for stable organic complexes [346]. Therefore, immediate Mg bioavailability depends mainly on the dynamic equilibrium between soluble and exchangeable Mg, rather than on the total mineral reserve.

Interactions with the exchange complex regulate Mg^{2+} retention and release. Mg^{2+} is electrostatically adsorbed onto negatively charged sites in clays and organic matter, contributing to soil cation exchange capacity [347]. However, Mg^{2+} is retained less strongly than other divalent cations, such as Ca^{2+} . It is also more vulnerable to competition with H^+ and Al^{3+} . In acidic soils, H^+ and Al^{3+} reduce Mg saturation in the colloidal complex and favor Mg displacement and leaching [342]. Thus, Mg bioavailability depends not only on total Mg concentration, but also on cationic equilibrium, base saturation, and soil exchange capacity.

Soil physicochemical conditions further determine the stability of Mg in the soil solution. The most relevant factors include pH, cation exchange capacity, electrical conductivity, and mineralogical composition [348]. Soil pH is particularly important. Acidic conditions increase competition between Mg^{2+} , H^+ , and Al^{3+} at exchange sites, reducing Mg retention. Less acidic conditions favor Mg persistence in exchangeable fractions [342]. BC application, especially when Mg-modified, can alter these conditions. In general, higher pyrolysis temperatures increase pH, ash content, exchangeable bases, and alkalinity, while decreasing the soluble organic matter fraction [340]. Since BC properties depend on feedstock and production temperature, their effects on Mg bioavailability can vary substantially.

A 180-day incubation study in acidic soil showed that Mg-modified BCs can improve soil chemical conditions, but their effect depends on feedstock and pyrolysis temperature [349]. Mg-modified BCs derived from rice straw and maize straw were produced at 300, 400, 500, and 600 °C. All treatments significantly increased soil pH compared with the control ($p < 0.05$). After 180 days, soil treated with Mg-modified rice straw-derived BC showed pH increases of 31.0–50.6%, depending on pyrolysis temperature. The material produced at 500 °C showed the strongest acidity-ameliorating effect at 60 and 120 days, whereas the material produced at 300 °C produced the highest pH on day 180. For Mg-modified maize straw-derived BC, soil pH increased over time, with increases ranging from 2.8 to 35.6%, depending on pyrolysis temperature and incubation period.

Exchangeable Mg also responded differently according to feedstock and pyrolysis temperature. In soils amended with Mg-modified rice straw-derived BC, exchangeable Mg tended to decrease as pyrolysis temperature increased. In contrast, soils treated with

Mg-modified maize straw-derived BC showed a general increase in exchangeable Mg during incubation. At 180 days, maize straw-derived BC increased exchangeable Mg by 13.0, 46.0, 10.9, and 28.7%, depending on production temperature [349]. However, this increase was not sufficient to shift the soil to a higher Mg fertility class. When effective Mg was classified as severely deficient ($<60 \text{ mg L}^{-1}$), deficient ($60\text{--}120 \text{ mg L}^{-1}$), or adequate ($120\text{--}300 \text{ mg L}^{-1}$), the maize straw-derived BC treatments remained within the deficient category [349]. This result is important because it shows that relative increases in exchangeable Mg do not necessarily translate into agronomically sufficient Mg supply.

Similar responses were observed in citrus orchard soil treated with citrus peel-derived BC and Mg-modified citrus peel-derived BC at application rates of 1, 2, and 4% during a 100-day incubation [350]. Soil pH increased by up to 2.78 units with the 4% application of Mg-modified BC, which was much higher than the increase observed with unmodified BC. Cation exchange capacity also increased significantly with application rate. At the end of incubation, Mg-modified BC increased CEC by 125.74, 165.85, and 207.80% relative to the control at the increasing doses [350]. This increase indicates a greater number of negatively charged sites capable of retaining Mg^{2+} and other cations. Therefore, Mg-modified BC may stabilize the exchangeable Mg fraction and reduce potential Mg loss through leaching.

These results show that Mg bioavailability is not a fixed soil property. It results from a dynamic balance among chemical fractions, competition within the exchange complex, and physicochemical conditions modified by management practices. Pyrolysis temperature, feedstock type, and BC application rate directly affect soil pH, cation exchange capacity, and exchangeable Mg concentration. However, higher pH or higher exchangeable Mg does not always guarantee sufficient Mg nutrition. The agronomic effectiveness of Mg-modified BC depends on whether the increase in labile Mg is large enough to overcome soil deficiency thresholds, persist over time, and remain accessible to plants under field conditions. Therefore, Mg-modified BC should be evaluated not only by its capacity to increase pH or exchangeable Mg, but also by its ability to maintain Mg availability within an agronomically adequate range while minimizing leaching and cationic imbalance.

4.6.3. Magnesium Adsorption and Desorption

Specific studies on Mg^{2+} adsorption and desorption in soil–BC systems remain limited, especially compared with the literature on phosphorus, heavy metals, and ammonium. Even so, recent evidence shows that BC can play a dual role. It can act as a reactive adsorption surface for Mg^{2+} , but it can also behave as a colloidal transport carrier under specific conditions. These processes depend on specific surface area, oxygen-containing functional groups, mineral content, cation exchange capacity, and particle size.

From a physicochemical perspective, Mg^{2+} adsorption onto BC occurs mainly through cation exchange and surface complexation with hydroxyl and carboxyl groups [347]. Mg-modified BCs usually show high alkalinity and greater cation exchange capacity, which increases the number of negatively charged sites available for cation retention [349]. For example, in citrus orchard soil treated with Mg-modified BC, cation exchange capacity increased by up to 207.80% relative to the control after 100 days of incubation, depending on the applied dose [350]. This increase suggests a greater potential to retain Mg^{2+} within the solid-phase exchange complex.

A more detailed mechanism was described in soil-column experiments using BC colloids derived from rice straw produced at 500°C [351]. These colloids had an average particle derived from rice straw produced at 500°C size of approximately 30 nm and a specific surface area of $110.6 \text{ m}^2 \text{ g}^{-1}$, which was ten times higher than that of bulk BC. FTIR and XPS analyses showed abundant oxygen-containing functional groups. The colloidal suspension had a pH of 7.08 and contained 52.6% C, 10.7% O, 0.51% Mg, 15.4% Fe, and

20.7% Al. These properties favored electrostatic interactions with Mg^{2+} and the formation of surface complexes.

In Mg transport experiments, BC colloids significantly increased the maximum Mg concentration in the effluent. In Mg-deficient soils, the maximum concentration increased from 5.83 mg L^{-1} without colloids to 8.18 mg L^{-1} with colloids. In Mg-enriched soils, it increased from 9.42 to 10.73 mg L^{-1} . Mass recovery was also higher in the presence of colloids, increasing from 13.3 to 16.9% in Mg-deficient soil and from 8.0 to 9.2% in Mg-enriched soil [351]. These results indicate that BC provides adsorption sites, but its colloidal fraction can also reduce net Mg retention by facilitating co-migration.

The adsorption process was adequately described by the Langmuir model ($R^2 > 0.900$), suggesting monolayer adsorption on specific sites. The kinetics followed a pseudo-second-order model. In addition, colloid-associated Mg showed a strong correlation with I cheeluted colloid concentration ($R^2 = 0.958\text{--}0.980$), confirming the role of particulate transport [351]. XPS analysis showed that the proportion of Mg present as $\text{Mg}(\text{OH})_2$ and MgCO_3 increased from 18.9% in the original BC to 46.0% in the recovered colloids. This confirms that new surface complexes formed during transport.

Hydrus-1D simulations further showed that BC colloids can increase Mg movement through the soil profile. During the first year, Mg migration reached 42 cm in Mg-deficient soil with colloids, compared with 35 cm without colloids. After five years, the cumulative Mg flux at 80 cm increased from 424.1 to 521.4 mg m^{-2} in the presence of colloids [351]. These findings show that Mg^{2+} adsorption onto BC does not necessarily result in stronger long-term retention. When BC particles move as colloids, adsorbed Mg can also be transported downward.

The available evidence indicates that Mg behavior in BC-amended soils is controlled by a balance between retention and mobility. On one side, BC can increase Mg^{2+} retention by improving cation exchange capacity and providing reactive functional groups [350]. On the other side, colloidal BC particles can enhance Mg^{2+} transport through surface complexation and co-migration. Therefore, Mg adsorption and desorption should not be evaluated only from the perspective of static retention. They should also be assessed in relation to BC particle size, colloidal stability, pyrolysis temperature, surface chemistry, soil texture, and flow conditions. This distinction is important because a BC that retains Mg^{2+} at the particle surface may still contribute to Mg redistribution or leaching if the colloidal fraction is mobile.

5. Conclusions

This review establishes a conceptual framework linking biomass type and pyrolysis conditions to soil macronutrient dynamics through their effects on BC physicochemical properties. Feedstock type determines the initial mineral composition, ash content, nutrient reserves, and structural features of BC, whereas pyrolysis temperature, residence time, and production conditions regulate carbon stability, porosity, alkalinity, surface area, and functional groups. These properties control nutrient adsorption, desorption, ion exchange, precipitation, microbial transformation, and gradual release. Therefore, BC functionality should not be considered a fixed property of the material, but the result of interactions among biomass origin, production conditions, soil properties, and nutrient-specific behavior.

The evidence reviewed shows that BC can improve the retention and availability of N, P, K, S, Ca, and Mg, but its effects are highly context-dependent. High-temperature BCs often show greater aromaticity, alkalinity, mineral concentration, and structural stability, which may favor nutrient retention and reduce leaching. However, they may also provide fewer labile functional groups or release fewer nutrients, depending on the feedstock

and nutrient considered. In contrast, BCs derived from mineral-rich biomasses, such as agricultural residues, animal wastes, sludge, and some urban wastes, can contribute more directly to nutrient supply and base cation availability.

A nutrient-specific interpretation is essential because each macronutrient responds through different mechanisms. N dynamics are influenced by adsorption–desorption, microbial transformations, and leaching control. P behavior depends on solubilization, precipitation, adsorption, desorption, and mineral-associated release. K availability is controlled by soluble and exchangeable pools, non-exchangeable K mobilization, and soil mineralogy. S, Ca, and Mg responses are linked to speciation, microbial activity, pH regulation, exchange reactions, and mineral interactions. Thus, total nutrient content alone is not sufficient to predict the agronomic value of BC.

The findings highlight the need to design BCs according to the nutrient limitations, pH, texture, mineralogy, organic matter content, and fertility status of the target soil. Integrating feedstock selection, pyrolysis optimization, post-production modification, and nutrient-specific mechanisms can support the development of tailored BCs for improving macronutrient availability, fertilizer-use efficiency, and long-term soil fertility. In this sense, BC represents a strategic tool for connecting biomass valorization with sustainable nutrient management and climate-smart agriculture.

6. Perspectives and Challenges

This review has conceptualized BCs as effective amendments for improving soil fertility due to their physicochemical properties and their capacity to regulate macronutrient dynamics. From a sustainability perspective, BCs also represent a promising strategy for biomass waste valorization, nutrient recycling, and the partial reduced dependence on synthetic fertilizers. However, concerns remain regarding the potential negative impacts that BC may exert on soil fertility and plant nutrition, as well as the formation or release of additional compounds that may be potentially harmful to human health and the environment [282]. Therefore, the sustainable use of BC requires balancing its agronomic benefits with environmental safety, long-term soil health, and the suitability of each material for specific soil-crop systems. In this context, the main challenges are centered on the following aspects:

6.1. Tailoring Production Conditions and Feedstock Selection

Both pyrolysis temperature and raw material significantly influence the effectiveness of BC in nutrient adsorption and desorption processes [352], BC characteristics differ considerably according to biomass nature and pyrolysis conditions; therefore, it is necessary to optimize production systems tailored to specific applications [167]. Biomass pyrolyzed at high temperatures exhibits greater surface area, higher aromaticity, and more advanced porous-structure development, which may favor physical nutrient retention and ion exchange in soil. In contrast, BCs produced at low temperatures retain a larger amount of oxygen-containing functional groups and mineral cations, which may increase their cation exchange capacity and direct contribution to the supply of nutrients such as K, Ca, and Mg. Therefore, not all BCs are equally effective in regulating macronutrient availability, making it necessary to select specific feedstocks and standardize production processes according to the agronomic objective [353], so that production conditions can be aligned with the intended purpose of BC application [354].

Beyond feedstock type and pyrolysis temperature, residence time and heating rate also influence BC functionality. Residence time can modify carbonization, aromatic condensation, surface area, pore structure, and mineral nutrient concentration, thereby affecting nutrient retention and release [355,356]. Heating rate also affects BC yield, ash content, fixed

carbon, pore development, surface charge, and the abundance of oxygen-containing functional groups, although pyrolysis temperature often remains the dominant control [91,356]. These variables should therefore be considered when designing BCs for specific nutrient-management objectives.

The pyrolysis atmosphere is another relevant production factor. Limited oxidative atmospheres can promote BC oxidation, increase microporosity, and enrich oxygen-containing functional groups such as hydroxyl (-OH) and carbonyl (C=O) groups. These changes may enhance surface reactivity and adsorption potential, although they can occur at the expense of BC yield [357]. Physical activation with CO₂ or steam may also increase pore development and surface area, but its agronomic value depends on whether these structural changes improve nutrient retention without excessively reducing nutrient-source potential.

Post-production modification can further support the development of tailored BCs. Acidification and oxidation may increase oxygen-containing functional groups and improve surface reactivity. Metal loading with Ca, Mg, Fe, or Al can enhance phosphate retention through precipitation, cation bridging, and ligand exchange. However, these modifications should be selected according to the target nutrient process, because highly activated or strongly modified BCs may shift from nutrient-supplying amendments toward adsorbent materials with lower nutrient-release capacity [358].

6.2. Practical Considerations for Biochar Application Under Different Soil Conditions

The agronomic performance of BC is strongly influenced by soil properties, particularly soil pH and texture. In acidic soils, BC often acts as a liming amendment due to its alkaline ash fraction and negatively charged functional groups, which can neutralize H⁺ ions and adsorb toxic Al³⁺, increasing soil pH and improving nutrient availability and root development [359]. Studies conducted in acidic soils have also reported increases in available P, K, Ca, and Mg, together with reduced aluminum toxicity and enhanced microbial activity [359,360]. However, excessive increases in soil pH may promote NH₃ volatilization when BC is co-applied with urea [176].

In alkaline and saline-alkaline soils, BC operates through different mechanisms. Its high porosity and cation exchange capacity promote Na⁺ adsorption, improve soil structure, and enhance water retention, thereby alleviating salt stress and supporting plant growth [359]. Furthermore, BC has been shown to reduce nitrate and ammonium leaching in calcareous soils without causing additional increases in soil pH [361].

Soil texture also determines the effectiveness of BC as a nutrient-regulating material. In coarse-textured or sandy soils, BC increases water-holding capacity and reduces the leaching of mobile nutrients, thereby improving nutrient use efficiency [359,362]. In contrast, in fine-textured or clay soils, BC can reduce compaction, increase macroporosity, and improve aeration and microbial activity, thereby promoting nutrient transformation and cycling [360,363]. Nevertheless, these changes may also alter nitrogen transformation pathways and, under certain management conditions, increase NH₃ losses [176].

6.3. Influence of Biochar Application Methods on Nutrient Dynamics

In addition to BC properties, its agronomic effectiveness is strongly influenced by application method, incorporation depth, application frequency, and co-application with fertilizers. Uniform incorporation within the plow layer (0–20 cm) increases contact between soil and BC particles, promoting the retention of P, K, Ca, and Mg and improving nutrient availability [360].

Incorporation depth significantly affects nitrogen dynamics. Placement of BC at depths of approximately 7.5–10 cm can act as an adsorptive barrier that reduces NO₃[−] and NH₄⁺

leaching by slowing downward water movement [361]. Likewise, deep placement may reduce NH_3 losses by inhibiting surface urease activity and delaying urea hydrolysis [364]. In contrast, surface applications can increase NH_3 volatilization by raising local pH and maintaining fertilizer concentration near the soil surface.

Application frequency also influences long-term nutrient dynamics. Repeated BC applications can increase soil organic carbon, improve K availability, and enhance nitrate retention. However, excessive annual applications may lead to the accumulation of soluble salts and chloride ions [359].

Finally, co-application of BC with mineral fertilizers generally improves nutrient use efficiency by increasing cation exchange capacity and reducing nutrient losses through leaching [176,362]. Nevertheless, the interaction between BC and nitrogen fertilizers is complex, as some studies have reported increased NH_3 volatilization due to pH elevation and enhanced urease activity in the fertilized zone [176].

6.4. Nutrient Availability and Crop Yield Responses

Reductions in yield have also been documented when high application rates or unsuitable materials are used. Karer et al. [365] observed that the application of wood-derived BC at 72 t ha^{-1} reduced maize and wheat yields by 46 and 70%, respectively, due to the immobilization of N and micronutrients under high-pH conditions. Similarly, Baronti et al. [366] reported that applications above 1.7% ($>60 \text{ t ha}^{-1}$) decreased ryegrass dry matter production, which was attributed to physicochemical alterations in soil. These results show that BC can be beneficial only when appropriate application rates and properly selected materials are used. Nevertheless, knowledge remains limited regarding the long-term sustainability of repeated applications and the maximum safe rates across different cropping systems [115].

6.5. Potential Environmental Risks of Biochar Use

According to a Safety [367], BCs can induce both positive and negative effects on plants and soil microorganisms, since the potential risks within the “BC–soil–plant” system remain incompletely understood [368]. Their high adsorption capacity, although beneficial for reducing nutrient losses through leaching, may also decrease the availability of essential nutrients and disrupt the nutritional balance of soil. When BCs exhibit high affinity for certain ionic species, temporary immobilization of nutrients such as N, P, or micronutrients may occur, affecting their uptake by roots. In addition, excessive retention may indirectly interfere with plant–microorganism communication by modifying the availability of compounds involved in symbiotic processes and rhizospheric dynamics [369].

Likewise, depending on production conditions, some BCs may modify the chemical speciation of nutrients or alter competitive relationships among cations, such as K^+ , Ca^{2+} , and Mg^{2+} , generating imbalances in plant uptake [352]. Therefore, it is essential to further evaluate the long-term behavior of BCs, particularly regarding their influence on nutrient availability, retention, and transformation across different soil types.

BC itself may also act as a potential source of contaminants, as feedstock composition and pyrolysis conditions can result in the presence of polycyclic aromatic hydrocarbons (PAHs) and potentially toxic elements, including Pb, Cd, Cu, Zn, Cr, Ni, Hg, and As. These compounds may interfere with soil microbial activity, nutrient mineralization, and nutrient uptake when they accumulate in amended soils. Waste-derived and manure-derived BCs therefore require careful characterization before agricultural application [355,358].

High-ash BCs may also increase soil electrical conductivity and contribute to salt accumulation after repeated applications. This risk is particularly relevant for mineral-rich materials, such as manure- and poultry litter-derived BCs, which may contain soluble salts

and high concentrations of K, Ca, Mg, and Na. Although these properties can improve nutrient supply in the short term, excessive or repeated application may increase salinity stress and reduce nutrient-use efficiency in sensitive soils or crops [358].

Preventive measures should include feedstock screening, contaminant analysis, application-rate adjustment, and periodic monitoring of soil pH and electrical conductivity. For high-ash BCs, lower application rates, site-specific management, and avoidance of repeated applications in saline or poorly drained soils may reduce salinization risks while preserving potential agronomic benefits.

6.6. Biochar for Long-Term Soil Health and Climate-Smart Agriculture

BC application as a soil amendment has mainly been evaluated under controlled laboratory, greenhouse, or small-scale experimental conditions. However, its field-scale implementation remains limited, partly because production costs continue to be a restrictive factor for its widespread adoption [279]. In this context, large-scale field studies are needed to validate its agronomic effectiveness under real conditions and across different soil systems [352]. Such studies should not only assess short-term improvements in nutrient availability or crop response but also evaluate the persistence of BC effects on soil structure, nutrient-use efficiency, carbon stabilization, water retention, and microbial functionality.

In addition, BC surface properties, including functional groups, adsorption capacity, and chemical reactivity, may change over time due to oxidation and microbial degradation processes associated with material aging [66,150]. These transformations may alter its capacity to retain and release nutrients, as well as its interaction with the soil microbiota. Consequently, specific studies on BC aging are essential to define appropriate application rates, evaluate its structural stability, and determine its long-term impact on soil properties and functions across different soil types [370]. This is particularly relevant because the agronomic performance of BC may change over time, shifting from an initially reactive amendment to a more stabilized component of the soil organic-mineral matrix.

From a climate-smart agriculture perspective, BC represents a promising tool because it can simultaneously contribute to soil fertility improvement, nutrient loss reduction, carbon persistence, and mitigation of environmentally harmful emissions. However, these benefits are not universal and depend strongly on feedstock type, pyrolysis conditions, application rate, soil texture, soil pH, climate, and crop nutrient demand. Therefore, BC should not be considered a generic amendment, but rather a soil-specific and purpose-oriented strategy.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/su18157930/s1>, Table S1: Influence of biomass type and pyrolysis conditions on the physicochemical properties of biochars derived from agricultural, woody, animal, urban, and aquatic biomasses; Table S2: Elemental composition of biochar derived from different biomass groups; Table S3: PRISMA 2020 Checklist. The checklist was prepared in accordance with the guidelines of [371].

Author Contributions: Conceptualization, K.B.Q.-S. and Y.Y.A.-P.; methodology, K.B.Q.-S.; software, K.B.Q.-S.; validation, K.B.Q.-S., Y.Y.A.-P. and M.J.M.-C.; formal analysis, K.B.Q.-S.; investigation, K.B.Q.-S.; resources, K.B.Q.-S., Y.Y.A.-P. and M.J.M.-C.; data curation, K.B.Q.-S.; writing—original draft preparation, K.B.Q.-S.; writing—review and editing, K.B.Q.-S., Y.Y.A.-P. and M.J.M.-C.; visualization, K.B.Q.-S.; supervision, M.J.M.-C. and Y.Y.A.-P.; project administration, K.B.Q.-S.; funding acquisition, Y.Y.A.-P. and M.J.M.-C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Ministerio de Ciencia, Tecnología e Innovación, through the Sistema General de Regalías (SGR) Project No. 100384 (BPIN 2021000100384).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study is available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

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