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Biochar and phosphogypsum in agricultural soils: Individual roles, combined potentials, and future prospects

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ABSTRACT

Soil degradation has become a pressing global issue, posing a significant threat to the soil environment, agricultural productivity, and food security. Factors such as nutrient depletion, erosion, and contamination have contributed to the declining health of soils worldwide. Biochar (BC) and phosphogypsum (PG) have shown great promise in improving soil fertility and quality, but their combined application and the full extent of their potential benefits and limitations remain underexplored and demand comprehensive attention. This review thoroughly assesses the individual applications of BC and PG as soil amendments, focusing on their respective physicochemical properties and their effects on soil structure, fertility, and plant growth. It also explores the synergistic effects of BC and PG when used in combination, emphasizing their potential to improve soil water retention, nutrient availability, and overall plant performance, thereby offering a promising solution for sustainable agriculture. Finally, the key considerations associated with the combined use of BC and PG, such as application rate, impact on soil health, and variability in soil types are addressed, while outlining future research directions to enhance their efficacy. In conclusion, the combined application of BC and PG contributes to impoved soil health and enhanced crop yields and promotes the integrated management of biomass waste and industrial byproducts such as PG, transforming agricultural and industrial waste streams into valuable resources, thus presenting a low-cost, environmentally sustainable approach to addressing soil degradation.

Key Words: crop growth, heavy metal remediation, nutrient availability, potentially toxic element, soil amendment, sustainable agriculture, synergistic effect

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INTRODUCTION

Soil functions as a complex system that intersects the atmosphere, lithosphere, hydrosphere, and biosphere, providing essential support for life on Earth and playing a vital role in society, ecosystems, and agriculture (Lehmann *et al*., 2020). Soil health is vital for crop yield, water quality, and climate change, thus significantly impacting food security and human survival (Hou *et al*., 2020). In recent years, because of unreasonable human activities (Mukherjee *et al*., 2014), global soil environmental issues such as soil acidification, salinization, compaction, fertility decline, and heavy metal pollution have become increasingly prominent (Oliver and Gregory, 2015; Qin *et al*., 2021). The methods for soil health improvement to ensure long-term productivity include physical methods, chemical methods, biological methods, and agricultural engineering measures (Dhaliwal *et al*., 2020; Khan *et al*., 2021), among which soil conditioners have received widespread research attention. Soil conditioners can enhance soil fertility by boosting moisture level, promoting active microbial populations, and facilitating plant nutrient absorption, as well as improving soil structure by stabilizing aggregates, adjusting bulk density, and optimizing air-water relationship within the soil (Garbowski *et al*., 2023), thereby improving crop yield and promoting sustainable agriculture. Notably, industrial and agricultural activities generate increasing amounts of wastes, such as plant residues, manure, and solid wastes, which are, at the same time, resources, and their use for soil improvement is a positive approach to mitigate the environmental risks associated with waste disposal (Tran *et al*., 2023).

Biochar (BC), often used as a widely used soil amendment, is a carbon (C)-rich organic substance produced by pyrolysis of biomass such as wood (Kumari *et al*., 2016), sewage sludge (Zong *et al*., 2018), animal manure (Gong *et al*., 2022), and plant residues (Boitt *et al*., 2018) under oxygen (O)-limited environments with temperatures ranging from 200 to 700 °C (Dai *et al*., 2017). Depending on various feedstock materials and pyrolysis conditions or use of additives, BC possesses specific properties such as low bulk density and high porosity, specific surface area (SSA), cation exchange capacity (CEC), and pH, making it suitable for enhancing soil health and thereby increasing

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crop productivity (Murtaza *et al*., 2021; Haider *et al*., 2022; Fornes *et al*., 2024). For example, the application of maize straw BC at the rates of 10, 20, 40, and 60 t ha^{-1} significantly improved soil conditions, including soil bulk density, porosity, and electrical conductivity (EC), compared with no BC addition (Li *et al*., 2018). The addition of cotton stalk-modified BC into surface soil at 12 Mg ha^{-1} significantly increased maize grain yield by 34% and wheat plant biomass by 25% compared with the control (El-Sharkawy *et al*., 2022). However, the contents of inorganic nutrients in BC, especially available phosphorus (P), still need to be improved (Buss *et al*., 2022). Adding fertilizer supplements to BC can enhance the contents of inorganic nutrients in BC. However, this will further increase the costs, thus reducing the potential benefits of BC doping. Combining BC with industrial wastes, *e.g*., red mud, phosphogypsum (PG), and steel slag, has demonstrated promising application prospects in terms of economic benefits and agricultural effectiveness (Chen *et al*., 2017; Huang *et al*., 2017; Gao and Goldfarb, 2019; Jing *et al*., 2019).

Phosphogypsum is an industrial solid waste generated in the wet production process of phosphoric acid (Wei *et al*., 2021). The main component of PG is gypsum or calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$), accounting for more than 90% of its mass, and the remainder includes soluble P, eutectic P, heavy metals, fluorides, organics, and radioactive elements (Rutherford *et al*., 1994). It is estimated that about 4.5–5.5 t PG is generated for every 1 t phosphoric acid produced worldwide (Mohammed *et al*., 2018), indicating that the amount of the byproduct PG exceeds that of the desired product. The storage of PG takes up large areas of land and damages the surrounding ecosystem due to the potentially toxic substances it contains (Silva *et al*., 2022). Therefore, PG disposal is an environmental problem that needs to be paid attention to. Given the importance of resource utilization of solid wastes and the nutrient elements contained in PG, there is growing interest in the utilization of PG in soil reclamation to mitigate soil erosion (Suleymanov *et al*., 2019), increase available sulfur (S) and P (Delgado *et al*., 2002), and improve soil structure and crop production (Nayak *et al*., 2009). da Costa *et al*. (2018) observed that adding PG increased the development of reproductive structures of maize and crambe, thus increasing grain yield. Additionally, the mixture of PG and lime showed synergistic effects on maize and bean growth, suggesting that the combined application of soil amendments has greater potential to improve soil fertility and promote crop growth.

The combined application of BC and PG offers significant benefits as a soil amendment. At present, studies have shown that BC can passivate the impurities such as heavy metals contained in PG and alleviate soil compaction caused by PG, while PG can neutralize the alkalinity of BC and enhance its nutrient content, thereby achieving better soil amendment effects than application separately (Peng *et al*., 2020). So far, however, relatively few studies have been conducted on the effects of combined application of the PG and BC on soil health and crop yield. The synergistic effects of these two substances have received little attention. Thus, this review i) focuses on the characteristics of BC and PG and their effects on soil properties and plant growth, ii) discusses the synergistic mechanisms of BC and PG application, their benefits to soil environment, and the potential of their combined application for soil improvement, and iii) emphasizes the challenges and prospects for the combined use of BC and PG.

To ensure a comprehensive and up-to-date review, we conducted a literature search using major databases, including Web of Science, Scopus, and Google Scholar. Keywords such as “biochar”, “phosphogypsum”, “soil”, “soil amendment”, “soil remediation”, “soil improvement”, “soil conditioner”, “soil application”, “agricultural soil”, “combined application”, and “biochar and phosphogypsum” were used. The review focused on peer-reviewed articles published between 2000 and 2024, encompassing both foundational studies and recent advancements. In total, more than 140 articles were analyzed and synthesized.

APPLICATION OF BC IN AGRICULTURAL SOILS

Adding BC to agricultural soils can change the properties of soil, including physical properties like soil bulk density, agglomeration structure, and water-holding capacity (WHC), chemical properties such as pH, nutrient content, and CEC, and biological properties such as microbial abundance, activity, and diversity (Ahmed *et al*., 2016; Zhang *et al*., 2021). The type and extent of such effect on soil are directly related to BC characteristics, which rely on the feedstock type and pyrolysis temperature (Mohd Hasan *et al*., 2019; Huang *et al*., 2021).

Properties of BC and influencing factors

Biochar, with an ordered lamellar structure, is a porous and highly aromatic C-rich solid substance produced through the pyrolysis of waste biomass or organisms under O-restricted conditions. The tiny particle size and porous structure of BC make its SSA large, ranging from 100 to 460 m^2 g^{-1} (Novak *et al*., 2009). During the pyrolysis process, various active functional groups are formed, providing BC with abundant surface active sites to adsorb pollutants (Lian and Xing, 2017). Moreover, the mineral components and O-containing functional groups on the surface of BC are usually alkaline, consequently making the pH value of BC in the range of 5–12 (Novak *et al*., 2009; Xu and Fang, 2015). Feedstock type and pyrolysis temperature are two factors that directly determine BC physicochemical properties and ultimately affect its improvement effect on soil fertility or remediation effect on soil heavy metal pollution (Laghari *et al.*, 2016; Tomczyk *et al.*, 2020).

Various feedstocks can be used for BC preparation, including agricultural and forestry wastes, such as wooden branches, crop straws, and vegetable leaves, industrial and domestic wastes, such as sewage sludge and kitchen wastes, and livestock and poultry manure, such as sheep manure and pig dung (Ahmad *et al.*, 2014). Biochar mainly includes ash and carbonaceous components, and the contents of these components vary with feedstock type. The ash contents and volatile matter of sludge and fecal BCs are usually higher than those of plant-based BCs (Zhang P Z *et al.*, 2019). Keiluweit *et al.* (2010) reported that the ash of BC prepared from animal manure was significantly higher than that of BC prepared from plant sources, and more minerals were retained in animal manure BC. Due to the positive correlation between ash and pH, manure and sludge BCs also exhibit higher pH and CEC values than plant-based BCs. The presence of alkali and alkaline metals such as potassium (K), calcium (Ca), sodium (Na), and magnesium (Mg) can enhance the formation of oxygenated functional groups on the surface of BC (Lu *et al.*, 2023). In addition, plant-based BCs have lower ash and volatile matter contents and more micropores due to the higher cellulose and lignin contents of the feedstock (Li *et al.*, 2014). The thermal decomposition process of cellulose, hemicellulose, and lignin promotes the development of channel structures that contribute to the formation of pore structures (Tomczyk *et al.*, 2020). Additionally, feedstock type also influences the elemental composition of BC. Compared with manure-based BC, crop-based BC exhibits a higher K content but lower Na, Ca, and Mg contents (Tag *et al.*, 2016). The pH, CEC, SSA, and elemental composition of BC influence its ion exchange with soil particles, affecting the characteristics of soils amended with BC.

Pyrolysis temperature has a great influence on the properties of BC, thus affecting its effectiveness in improving soil properties (Ding *et al.*, 2014). When pyrolyzed at a low temperature of 200–400 °C, BC contains more O-containing functional groups (*e.g.*, carboxyl, hydroxyl, carbonyl, phenolic hydroxyl, and aldehyde groups), which not only promote the adsorption of heavy metals and the passivation of inorganic contaminants but also stimulate nutrient exchange and accumulation in soils (Huang *et al.*, 2021). As pyrolysis temperature increases, volatile substances are progressively released, leading to the formation of more pores and a larger SSA (Lataf *et al.*, 2022). The porous structure and large SSA help BC maintain a high WHC, thereby improving soil properties when applied to soil (Glaser *et al.*, 2002). Besides, the accumulation of non-pyrolytic inorganic minerals increases the ash content of BC, which contributes to a higher pH. The increase in alkaline functional groups and the reduction in acidic functional groups also contribute to the higher pH of BC (Kim *et al.*, 2013).

When pyrolyzed at a temperature of 400–500 °C or even higher, BC will undergo dehydration, polycondensation of aliphatic hydrocarbons, removal of polar functional groups like hydroxyl and carboxyl groups, and dehydrogenation, which lead to a BC product characterized by a more condensed aromatic structure and greater stability (Ralebitso-Senior and Orr, 2016; Mandal *et al.*, 2021). The removal of functional groups and formation of aromatic C will reduce the CEC of BC, thus limiting its ability to regulate the contents and availability of nutrients and heavy metals in soil through adsorption and release processes. In summary, increasing the pyrolysis temperature raises the ash content, pH, and SSA, while reducing the CEC and abundance of surface functional groups of BC.

Effects of BC on soil properties

Applying BC to soil can change the physical properties of soil, including soil density, structure, and WHC. Bulk density is a fundamental physical property of soil (Nawaz *et al.*, 2013). The bulk density of BC is much lower than that of soil due to the porous structure of BC, so adding BC helps reduce soil bulk density, thus improving soil permeability (Omondi *et al.*, 2016). Moreover, BC has a large SSA and numerous negative charges, which can improve soil CEC, thereby promoting the formation of soil aggregates (Kinney *et al.*, 2012; Borchard *et al.*, 2014). For instance, Liu *et al.* (2014) found that the application of BC at 40 t ha^{-1} improved the mean weight diameter of water-stable soil aggregates by 28%, compared with the control treatment. The WHC of BC mainly depends on its porous structure and the presence of O-containing functional groups. The acidic groups, including hydroxyl and carboxyl groups, on the surface of BC carry negative charges, which enhances the adsorption potential of BC and thereby increases soil WHC (Suliman *et al.*, 2017).

Application of BC also significantly affects the chemical characteristics of soil, such as pH and CEC. Biochar is generally alkaline and commonly used in acidic soils to raise soil pH (Zong *et al.*, 2018). Also, base cations like Na^+, K^+, Ca^{2+}, and Mg^{2+} present on BC surfaces can exchange with hydrogen (H^+) and aluminum (Al^{3+}) ions in the soil. This not only leads to an increase in the base cations, thus raising soil pH and but also improves nutrient levels and decreases Al toxicity (Steiner *et al.*, 2007; Van Zwieten *et al.*, 2010). Due to the presence of alkaline oxides, carbonates, silicates, and functional groups in BC, Al^{3+} can be converted into the less toxic aluminum hydroxide through precipitation or complexes *via* specific adsorption (Dai *et al.*, 2017), thereby reducing its toxicity to plants and promoting crop production. Additionally, because of the high SSA and negative charges of BC, the CEC of the amended soil can be efficiently increased (Lehmann *et al*., 2011; Jaafar *et al*., 2015). Typically, high CEC corresponds to high nutrient contents. Guo *et al*. (2012) showed that BC with a high CEC was conducive to retaining a greater amount of nutrients and minimizing nutrient leaching in soil. However, a study in the Coastal Plain of USA observed that adding pecan shell-based BC to a loamy sand had little effect on soil CEC but increased soil pH and total organic C, P, Ca, K, and manganese (Mn) levels (Novak *et al*., 2009). Modification or compounding of BC with other materials is often a promising method to improve the effect of BC as a soil amendment (Haider *et al*., 2022).

Different microbial populations live in soil, and the application of BC changes the microbial community structure by improving the physical and chemical properties of the soil, thus improving soil fertility and crop yield (Lehmann *et al*., 2011). For instance, rice straw BC has a high labile C content. Its application increases microbial activities, thereby enhancing the biological fertility of degraded soils (Purakayastha *et al*., 2015). The pore structure of BC provides abundant sites for microbial survival, helps maintain high microbial populations, and mitigates greenhouse gas emissions from the soil (Compant *et al*., 2010). Additionally, BC positively influences soil enzyme activity, which is an indicator of soil quality. Studies have displayed that BC can significantly increase the activities of dehydrogenase and urease in soil, thereby enhancing soil quality (Ameloot *et al*., 2013; Mierzwa-Hersztek *et al*., 2016).

Effects of BC on plant growth

By enhancing soil properties, higher crop yields can be achieved *via* BC application. Biochar can increase soil aggregate stability, porosity, WHC, nutrient contents, pH, and CEC and reduce soil bulk density, which is beneficial for crop production. When applied in a sandy loam soil, BC increased soil CEC, organic matter, available P, and exchangeable Mg, Ca, and K, promoting nutrient absorption by maize and improving crop yield (Minardi *et al*., 2017). Abujabhah *et al*. (2016) added BC prepared from Acacia green waste to an orchard soil at 47 t ha^{-1} before planting, and they found greatly increased in soil organic matter and changed soil community structure, which promoted crop production. Yamato *et al*. (2006) conducted a field study in South Sumatra, Indonesia. The results showed that incorporating BC at 37 t ha^{-1} improved soil chemical properties, created favorable conditions for root growth, and promoted the growth of mycorrhizal fungi as well as maize, peanut, and mango.

Acidic or acidifying soils typically exhibit low fertility because of the higher availability of Al and Mn and reduced availability of P, Ca, and Mg. Adding BC to acid soils can neutralize soil acidity and enhance crop biomass or yield by 28%–363% (Yu *et al*., 2019). Additionally, the alkaline components in BC can react with harmful metals like Al and Mn in the soil to form precipitates or complexes, reducing their bioavailability and toxicity. However, BC affects alkaline soils differently, and studies on BC for plant growth in alkaline soils are relatively rare. The reason is that in alkaline soils, the effect of alkaline BC in reducing soil pH is ineffective, and plant growth is limited by the high pH and the low availability of nutrient elements. Therefore, it is necessary to develop acid-modified BC or acidic BC-based composites for the amelioration of alkaline soils. Mao *et al*. (2022) used BC, PG, and earthworm manure as soil conditioners. They found that the free phosphoric acid and Ca^{2+}, which can react with the carbonate in PG, could lower the pH of saline-sodic soils.

Biochar is an excellent amendment for heavy metal-contaminated soils. It alters heavy metal speciation in soil, immobilizes heavy metals, and reduces their bioavailability and mobility in soil, thereby improving plant growth (Mosa *et al*., 2016; Zama *et al*., 2018). For example, Jiang *et al*. (2020) reported that addition of Litchi branch BC at 30 t ha^{-1} greatly improved soil pH, CEC, and organic matter content while alleviating the accumulation of lead (Pb) and cadmium (Cd) in the crops (cucumber, sweet potato, and rape), thereby increasing the crop yields up to twofold compared with the untreated group. To further improve the heavy metal passivation ability of BC, it is often modified with suitable materials. Weng *et al*. (2020) reported that the combined application of bagasse BC and red mud reduced the proportions of active Cd, zinc (Zn), and copper (Cu) while increasing their stable proportions in the soil. By changing their chemical speciation, BC reduced the bioavailability of these heavy metals and, in turn, their contents in the roots of *Eucalyptus*, thus increasing the biomass of *Eucalyptus*.

APPLICATION OF PG IN AGRICULTURAL SOILS

Phosphogypsum can directly or indirectly improve agricultural soils by reducing Al toxicity *via* displacing Al^{3+} from soil colloids with Ca^{2+} and precipitating it with sulfate ion (SO_4^{2-}), improving soil physical structure by promoting clay flocculation and aggregate stability through Ca^{2+} addition, ameliorating saline-sodic soils by providing Ca^{2+} to replace exchangeable Na^+, which is then leached, thereby reducing soil pH and alkalinity, and promoting nutrient uptake in plants by improving soil nutrient availability (Suleymanov *et al*., 2019; Duart *et al*., 2021; Hanafi *et al*., 2021; Michalovicz *et al*., 2021). However, PG typically contains potentially toxic elements (PTEs) and naturally occurring radioactive material (Guerrero *et al*., 2021), limiting its utilization in agriculture. Despite these challenges, PG can be a valuable resource for soil improvement and crop yield increase if adequately treated.

Properties of PG

Phosphogypsum is a grey and damp acidic byproduct from the wet process production of phosphoric acid. Its particles are fine, with a maximum size of 0.5–1.0 mm. In terms of particle size distribution, 50%–75% of the material consists of particles finer than 0.075 mm, giving it a texture similar to silt or silty sand (Es-Said *et al*., 2020). Phosphogypsum primarily comprises gypsum, constituting over 90% of its mass. Compared with gypsum, using PG for soil remediation is more cost-efficient and more effective (Huang *et al*., 2022; Qi *et al*., 2023). Phosphogypsum has a large SSA. Therefore, it has a strong adsorption capacity for pollutants. The high solubility of PG (approximately 250 mg L^{-1}) offers rich nutrients, such as P, S, Ca, and K, thereby increasing soil fertility and promoting plant growth (Duart *et al*., 2021). However, PG also contains trace metals, which can accumulate to high concentrations and pose risks to soil (Rutherford *et al*., 1994). The pore water retained within the interstitial spaces of PG crystals typically contains significant residual amounts of phosphoric acid, sulfuric acid, and hydrofluosilicic acid, contributing to the acidity of PG (Luther *et al*., 1993). Therefore, to enable its resourceful reuses, it is essential to treat PG appropriately to reduce its toxicity (*e.g*., acidity and heavy metal content).

Effects of PG on soil properties and plant growth

Phosphogypsum has been extensively used in agricultural soils, serving not only as an additive to enhance soil properties but also as an amendment for saline/alkaline soils and as a source of nutrients for plant growth (Huang *et al*., 2022; Silva *et al*., 2022). Its application can improve soil aggregation, microbial biomass C, organic C, and aggregate-associated C and reduce soil pH and exchangeable Na percentage, thereby increasing hydraulic conductivity and moisture retention capacity of the soil, leading to increased crop yields (Nayak *et al*., 2013; Araújo *et al*., 2019). Silva *et al*. (2022) showed that applying PG promoted tomato growth, photosynthetic function, and yield due to the increased Ca and P availability in soil. Duart *et al*. (2021) found that applying PG increased Ca^{2+} and SO_4^{2-}-S in the 0–0.60 m soil layer and P, K, Ca, and S levels in the rice flag leaves, thus increasing rice yields by 10%–11% with a PG dosage of about 4 Mg ha^{-1}.

Soil acidification has become a growing global problem, primarily driven by intensive agricultural practices, notably the excessive use of ammonium-based fertilizers. Atmospheric acid deposition also contributes to this process. Acidic soil can cause toxic elements like Al and Mn to dissolve, which inhibits plant root growth and decreases the availability of essential nutrients like Ca and Mg. Phosphogypsum application can reduce the concentration of mobile Al (Churka Blum *et al*., 2013). Carvalho and van Raij (1997) reported that in the PG-treated soil, the formation of aluminum sulfate cation, aluminum monofluoride cation, aluminum difluoride cation, and aluminum fluoride reduced the activity of Al^{3+}. By supplying Ca, PG can greatly promote crop root development and increase crop yield. Since PG is inherently acidic, some researchers have mixed it with alkaline material to reduce its acidity and optimize its effect on acidic soil. For example, Lee *et al*. (2009) added calcium hydroxide into PG, and the modified PG improved the availability of P, S, K, Ca, and Mg in soil and, in turn, improved microbial biomass C and nitrogen (N) concentrations, soil enzyme activity, and plant growth compared with unmodified PG.

Saline soils contain high levels of sodium sulfate and sodium chloride, causing poor soil structure, aeration, and permeability. Alkaline soils have high sodium carbonate, sodium bicarbonate, and pH (8.8–10) levels but a low P content, which is unfavorable for crop growth (Qi *et al*., 2023). Phosphogypsum can be used as a chemical amendment for the remediation of saline-alkaline soils, which is cost-effective and requires no pre-treatment (Huang *et al*., 2022). About 0.6 million tons of PG is used annually in agricultural soils in the USA, where it can improve water flow in saline-alkaline soils and supply essential Ca in alkaline soils (Papastefanou *et al*., 2006). Moreover, the abundant Ca^{2+} in PG can effectively replace Na^{+} in soil, making PG a promising material for reducing soil salinity (Burrow and Surapaneni, 2004). The acidity of PG can effectively neutralize the alkalinity of the soil. For example, Jiang *et al*. (2015) developed a nanocomposite soil conditioner consisting of bumpy clay, PG, sodium polyacrylate, and weathered coal. It was combined with conventional fertilizers to treat saline soils. This method effectively lowered soil salinity and alkalinity through ion exchange, deactivation, and pH adjustment mechanisms, thus fostering crop development and enhancing the salt tolerance of plants. Al-Enazy *et al*. (2018) evaluated the effects of PG alone and its combination with plant growth-promoting rhizobacteria on maize grown in a saline soil. The results indicated that applying PG reduced soil pH but decreased soil available K content, and maize showed a marked increase in dry biomass (82%–127%) and nutrient absorption. Smaoui-Jardak *et al*. (2017) also demonstrated that the addition of PG in saline-alkaline soils can significantly reduce soil EC. Specifically, after adding 80% PG, soil EC decreased by 26%.

Soil contamination with heavy metals has become increasingly prominent. Heavy metals such as Pb, Cd, Cu, arsenic (As), and chromium (Cr) can enter and accumulate in soils through various pathways, resulting in soil degradation and affecting crop safety and human health (Xie *et al*., 2022). The mechanism of PG improving heavy metal-contaminated soil involves heavy metal precipitation and their adsorption onto soil colloids. Therefore, their activity, mobility, and bioavailability to plants are reduced (Qi *et al*., 2023). Moreover, the fluorine (F) in PG can form a metal-F complex to passivate the heavy metals in soil. Research by Batukaev *et al*. (2017) demonstrated that applying PG at 10–40 t ha^{-1} in Krasnodar Krai land led to a 57% reduction in Cd^{2+} concentration in the soil. A study carried out by Mahmoud and Abd El-Kader (2015) revealed that the application of PG alone or combined with rice straw compost (PG+CP) reduced the uptake of Pb, Cd, and Zn by canola plants and plant dry biomass, and PG+CP led to more significant improvement in crop production than single PG. Interestingly, the addition of PG alone resulted in a more pronounced immobilization of heavy metals than PG+CP. Also, Outbakat *et al*. (2022) demonstrated that potentially leachable contaminants in PG would not cause harmful effects on the environment when PG was applied at a low rate.

However, researchers hold different views on the impact of PG on soil health. When PG is applied excessively, the heavy metals and radioactive elements in it may contaminate the soil. Smaoui-Jardak *et al*. (2017) reported that the Cd, Zn, and Cr levels in the different parts of tomato plants increased with increasing application of PG. When PG was added at a very high rate, Cd concentration in tomato exceeded the recommended maximum allowable concentration. Akfas *et al*. (2024) pointed out that the residual acidity and hazardous materials such as heavy metals and radioactive elements must be taken into consideration when applying PG for soil improvement.

COMBINED APPLICATION OF BC AND PG IN AGRICULTURAL SOILS

Studies have shown that the combination of BC and inorganic amendments can immobilize heavy metals in polluted soils mainly due to the precipitation of heavy metals in the form of phosphates, carbonates, or hydroxides (Betts *et al*., 2013; Sun *et al*., 2014). As an inorganic amendment, PG is rich in P and other essential elements for plant growth, such as S, Ca, silicon (Si), and iron (Fe). Recently, growing evidence shows that BC and PG can compensate for each other's limitations. Biochar can reduce the release of PTEs from PG, while PG can provide nutrients. The pH of the BC-PG mixture can be optimized by adjusting the ratio of these two materials to achieve greater improvement in soil quality and plant growth than the application of BC and PG alone.

Synergistic effects between BC and PG

Mixing BC with PG to form a composite amendment can improve the performance of BC in soil remediation. The addition of PG can improve the EC of BC and promote cation exchange on BC surface, thus enhancing its heavy metal adsorption capacity. The introduction of PG can also improve the H/C ratio of BC and bring abundant O- and Ca-containing functional groups to BC, which can further enhance heavy metal adsorption and immobilization (Chen *et al*., 2019). In the case of sewage sludge BC, although it improves soil fertility and C sequestration, it contains higher levels of heavy metals than agricultural or forestry waste BC, posing a potential risk (de Figueiredo *et al*., 2021). Phosphogypsum can be used as a heavy metal stabilizer to fix heavy metals in sewage sludge BC. The addition of PG can increase the functional groups such as carboxyl, phenol, hydroxyl, amine, and quinine groups, thus passivating heavy metals like nickel (Ni), Zn, Pb, and Cd (Huang *et al*., 2017). The surface of BC presents electronegativity. When BC is combined with PG, the PG-BC composite is positively charged under acidic conditions, enabling the adsorption of negatively charged heavy metal oxyanions such as $Cr_2O_7^{2-}$ and $HCrO_4^-$ (Lian *et al*., 2019).

However, the PTEs in PG are an important factor limiting its agricultural application. Biochar demonstrates a high adsorption capacity for heavy metals and other inorganic matters due to its high SSA and diverse array of surface functional groups, both non-polar and polar (Kammann *et al*., 2015). Peng *et al*. (2020) showed that the surface functional groups of rice husk BC effectively immobilized PTEs, including mercury, Pb, Cd, As, and F, from the leachate of PG through precipitation and complexation. In addition, when combined with BC, PG is aggregated and fully dispersed on the surface of BC, increasing the interaction between BC-PG and metal ions (Guo *et al*., 2023). The addition of PG can enhance the overall nutrient content of the BC-PG composite. Karim *et al*. (2019) reported that the BC-PG composite they prepared had higher calcium sulfide and potassium sulfate (K_2SO_4) contents and less leaching of F and heavy metals compared with single PG and BC. Furthermore, Si, Ca, and Mg contained in PG further enhanced the immobilization of heavy metals by BC in soil, indicating that BC-PG composite is very promising for soil application. Similarly, Vimal *et al*. (2022) co-pyrolyzed banana stalk biomass (BP), poultry litter (PL), and PG at 700 °C for 1 h to produce an alkaline BP-PL-PG composite enriched with K, P, and S. The results found that K in BP and S and Ca in PG were retained and enriched by forming K_2SO_4 and $CaSO_4$. Also, due to the formation of potassium phosphate during co-pyrolysis, BP-PL-PG contained a high level of soluble P, which improved nutrient utilization and promoted plant seed germination.

Phosphogypsum can be used to ameliorate soil salinization. However, for heavy saline soil with a high salt content, poor ground strength, and poor permeability, it is difficult to achieve satisfactory soil quality improvement by applying

PG only. Combination with materials such as BC often can achieve better results in the agricultural application of PG. Yoo *et al.* (2018) found that washing contaminated soil with ferric nitrate and [S, S]-ethylenediamine disuccinate increased the mobility of residual Pb and Cu, and subsequent stabilization with BC and PG alleviated this problem and increased the availability of K and P, which is beneficial for restoring soil health. Zhang X D *et al.* (2019) applied a mixed soil amendment at 22 500 kg ha^{-1} PG, 105 m^3 ha^{-1} cow manure, 3 750 kg ha^{-1} humic acid, and 45 m^3 ha^{-1} corn BC to explore its effect on salt reduction and soil property improvement in coastal saline soil. The results showed that this treatment reduced soil pH from 8.62 to 7.2–8.1, increased soil organic matter by 182%, and enhanced alkaline-hydrolyzable N content by 130%. Peng *et al.* (2020) used rice husk BC as a fertilizer amendment to mitigate PTEs in PG-amended soils. The results showed that compared with PG alone, the rice husk BC + PG treatment increased soil nutrient content, reduced F, As, and heavy metal levels, and boosted lettuce and asparagus yields by 56% and 605%, respectively. Furthermore, it decreased As, F, Cd, and Pb by 39%, 41%, 75%, and 86%, respectively, in lettuce and 100%, 64%, 75%, and 88%, respectively, in asparagus, which is crucial for agricultural production and food security. Elbagory *et al.* (2024) reported that co-applying PG with modified cotton stalk BC significantly enhanced soil organic C, CEC, and the availability of N, P, and K in a sandy loam soil. Both wheat grain and straw yields increased by up to 59%. Principal component analysis indicated a synergistic effect, with PG contributing Ca and S, and BC improving soil structure and nutrient retention, jointly supporting soil rehabilitation and crop productivity.

Since BC and PG are alkaline and acidic, respectively, changing the ratio of BC to PG can yield soil amendments of various pH values for soils of various pH levels. For instance, Panda *et al.* (2022) prepared banana stalk biomass-PG composite (BPC) by co-pyrolysis at 700 °C and investigated its application in acidic red soils. The results showed that during the incubation time, soil pH in the PG-treated group ranged from 2.3 to 4.6, whereas the BPC treatment increased soil pH to 7.7–8.6, thereby reducing soil acidity. In terms of nutrients, adding PG increased the available S content in soil leachate, making the acidic red soil more fertile. In addition, PG application facilitated the mitigation of Al toxicity due to the presence of Ca^{2+} and SO_4^{2-}, and BPC immobilized heavy metals in the soil and reduced their leaching. Mu *et al.* (2024) applied maize straw BC and PG to Cd-contaminated acidic red soil. At a combined application rate of 3 000 kg ha^{-1}, soil pH increased by 0.27 units, and available N, P, and K rose by 16%, 23%, and 9%, respectively. Available Cd in soil decreased by 17%, while Cd accumulation in pak choi was reduced by 49%. Moreover, soluble sugar, vitamin C, and chlorophyll contents in the plant increased by 10%, 15%, and 13%, respectively. A field experiment conducted by Mohamed *et al.* (2024) at El-Gemmieza Agriculture Research Station in Egypt demonstrated that the combined application of BC and PG significantly improved soil properties compared with their individual use. Physically, saturated water content, field capacity, hydraulic conductivity, and aggregate stability were enhanced. This was attributed to the improvement of soil structure and porosity by BC, along with the contribution of Ca^{2+} and SO_4^{2-} from PG to aggregate formation, structural stability, and pore connectivity. Chemically, co-application increased the availability of N, P, K, Ca, and Mg, optimized soil pH, and enhanced CEC and nutrient supply. Moreover, the combined application alleviated water stress, improved photosynthetic efficiency, and increased antioxidant enzyme activity in maize, resulting in a 20% increase in maize yield.

The effects of the combined application of BC and PG on agricultural soil are summarized in Table I. This combination improves soil properties such as pH, available nutrients (*e.g.*, Ca, S, P, K, and Mg), and organic matter content and reduces the mobility of heavy metals. It also enhances crop growth and yield by providing a balanced soil environment, addressing constraints specific to saline-alkaline, loamy or sandy, and acidic soils, and mitigating the phytotoxicity of toxic elements, which are critical for improving soil health and agricultural productivity.

The costs associated with producing and applying soil amendments are the key to transitioning this technology from laboratory or pilot scales to broader implementations. Currently, the global BC market is growing rapidly, driven by its applications for C sequestration, sustainable agriculture, and soil remediation. In 2023, the global BC market was valued at approximately US$541.8 million and is projected to reach US$1.35 billion by 2030, with a compound annual growth rate of 14% between 2024 and 2030 (Grand View Research, 2023). The ability of BC to enhance soil health and increase crop productivity has been a key factor in accelerating market adoption. In Europe, Austria and Switzerland have recently introduced the European Biochar Certificate, which permits the direct incorporation of BC into agricultural soils (Singh *et al.*, 2025). In rural regions of China, Japan, Brazil, and Mexico, BC production is largely driven by collaborative projects among research institutions and local organizations (Shi *et al.*, 2021). However, due to the high cost of producing high-quality BC, several companies have exited the market in recent years.

The global annual production of PG is estimated at 200–250 million tons (Jalali *et al.*, 2019). Due to the lack of continuous or direct utilization strategies, PG stockpiling has become an increasingly serious environmental concern. According to recent reports, PG stockpiles have reached

TABLE I

Effects of combined application of biochar (BC) and phosphogypsum (PG) on soil properties

BC or BC feedstock	Preparation or application method	Soil	Effects[a)]	Reference
Banana stalk biochar	Co-pyrolysis at 700 °C	Acidic red soil	Increasing soil pH and available S, reducing Al toxicity, immobilizing heavy metals	Panda *et al*., 2022
Maize straw BC	Co-pyrolysis at 500 °C	Cd-contaminated acidic red soil	Increasing soil pH and available N, P, and K, decreasing available Cd	Mu *et al*., 2024
Rice husk BC	Mixing pyrolyzed BC and dried PG	Loamy or sandy soil	Increasing nutrient content, reducing F, As, and heavy metals	Peng *et al*., 2020
Cotton stalk BC	Sequential application of PG followed by H_2SO_4-modified BC	Sandy loam	Increasing SOC, CEC, N, P, and K, improving soil structure	Elbagory *et al*., 2024
Plant-based BC	Sequential application of PG followed by pyrolyzed BC	Loamy soil	Increasing water content, field capacity, hydraulic conductivity, aggregate stability, and available N, P, K, Ca, and Mg	Mohamed *et al*., 2024
BC of sewage sludge and waste sawdust mixture	Mixing	Pd/Cu-contaminated soil	Increasing available K and P	Yoo *et al*., 2018
Cow manure BC	Mixing	Coastal saline soil	Decreasing soil pH, increasing soil organic matter and alkaline-hydrolyzable N	Zhang P Z *et al*., 2019

[a)] SOC = soil organic C; CEC = cation exchange capacity.

30 million tons in Republic of Korea (Yang *et al*., 2021), 55 million tons in Ukraine (Chernysh *et al*., 2021), and over 400 million tons in China (Ma *et al*., 2020). The USA currently holds the world's largest PG stockpile, exceeding 1 billion tons. Overall, global PG stockpiles are estimated to surpass 6 billion tons (Awad *et al*., 2024). Given the growing volume and associated environmental risks, increasing attention has been paid to the resource-efficient and market-driven reuse of PG. In Tunisia, field trials have shown that applying PG to degraded soils significantly improves crop germination and yield without exceeding safety limits for radioactivity (Gabsi *et al*., 2023). In Morocco, pot experiments have demonstrated the feasibility of using PG mixed with phosphate sludge and sewage sludge to restore degraded mining soils and enhance crop productivity. These findings highlight the potential for large-scale PG reuse in mine site reclamation, supporting its market valorization in arid and semi-arid regions (Guéablé *et al*., 2021).

However, few studies have explored the economic feasibility of combining BC and PG in agricultural soils (El-Naggar *et al*., 2019). The production cost of BC is related to various factors such as the source of raw materials, production conditions (technology and preparation system), type and price of energy used for pyrolysis, and labor expenses (Gueret Yadiberet Menzembere *et al*., 2023). As mentioned above, BC has a wide range of raw material sources, such as fast-growing plants with low nutrient requirements, making the feedstock cost of BC very low. According to Chen *et al*. (2021), a composite of pig manure, ferrous sulfate, and maize straw BC (PFMB) mixed in a 2:1:1 ratio requires only minimal stirring costs. The total expense for producing 1 t of PFMB is estimated at 1 738 RMB, significantly less than that of 1 t of maize straw BC alone. Zhang P Z *et al*. (2019) used PG, cow dung, humic acid, and corn straw as the raw materials for a composite soil amendment for salt reduction in muddy coastal saline soils. They found that the cost of the composite ranged from 2.55 to 6.01 RMB m^{-2}.

Only about 15% of PG is utilized as construction materials, cement additives, agricultural soil amendments, and others. The remaining 85% is either landfilled or discharged into water bodies, leading to serious resource wastage and environmental concerns (Jalali *et al*., 2019). Research by Guéablé *et al*. (2021) found that the addition of 65% PG to mining soils increased soil P and crop yield. Peng *et al*. (2020) conducted an economic evaluation based on the prices of soil amendments and the resulting vegetable yield. They found that, compared with the control, the yields of water spinach under the application of rice husk BC and rice husk BC+PG increased by 14% and 56%, respectively, with revenue increasing by US\$2.28 kg^{-1} BC and US\$9.35 kg^{-1} BC, respectively, which means that rice husk BC+PG resulted in higher economic benefits than rice husk BC alone. Thus, PG application in agricultural soils is an attractive and economically viable approach to reduce and reuse this industrial waste.

In summary, using BC-PG compositeas a soil conditioner has the advantages of realizing the reuse of industrial and agricultural wastes and reducing the cost of soil amendments. Its potential soil application advantages require further exploration by environmental and economic researchers.

Challenges

The combined application of BC and PG can compensate fortheir respective deficiencies and fully utilize their advantages, showing great potential in agricultural soil improvement and heavy metal pollution remediation. However, their combined application still has limitations and challenges. The composition of BC varies with raw material and pyrolysis temperature. Compared with BC derived from green waste, BC produced from sludge and animal manure contains heavy metals such as Pb, Cd, Cu, Mn, Zn, Ni, and Cr, as well as polycyclic aromatic hydrocarbons adhering to its surface, which limit the application of BC in soils (Freddo *et al*., 2012; Zheng *et al*., 2019). Furthermore, BC produced at a lower temperature contains toxic compounds that may be detrimental to soil and plant health (Pathy *et al*., 2021). Long-term application of BC may release potential heavy metals from within its structure through aging and degradation processes, thereby causing secondary contamination in the soil environment. When combined with PG, this risk should be carefully considered due to the possible cumulative effects of contaminants from both amendments.

Phosphogypsum contains impurities such as radioactive elements (*e.g.*, ^{226}radium, ^{222}radon, and ^{238}uranium) and heavy metals (*e.g.*, Cd, Pb, and Cr), so the frequent use of large amounts of these untreated industrial byproducts can contaminate the soil environment, damage plants, and pose risks to food safety (Lütke *et al*., 2020). It is also worth noting that the soluble F in PG may contaminate soil and waters. When entering human body along the food chain, F can cause lesions in human teeth and bones. Enamorado *et al*. (2014) carried out an extensive investigation into the absorption of 25 elements, including Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, and Pb, by tomato grown in soils treated with PG. The results showed that at a higher PG dosage, soil Cd concentration increased most significantly, and higher Cd concentrations in tomato shoots and fruits were observed. Despite these concerns, multiple studies suggest that the co-application of PG with BC may help mitigate certain environmental risks. The high SSA, porosity, and abundance of O-containing functional groups of BC allow it to adsorb and immobilize heavy metals and radionuclides through complexation, precipitation, and surface binding (Park *et al*., 2011). Thus, combining PG with BC not only enhances nutrient availability but also reduces the potential bioavailability and mobility of harmful PG-derived contaminants in soils. This strategy offers a rational approach to valorizing PG in a safer and more environmentally responsible manner.

Biochar has been commercialized and is readily available in most developed countries (Lin *et al*., 2025; Meena *et al*., 2025). In the Netherlands, Shell plc (formerly Royal Dutch Shell), an energy and petrochemical company, has utilized BC as a soil amendment through the integration of hydrolysis and hydroprocessing technologies (Senadheera *et al*., 2025). However, the promotion of BC in developing countries has not been so optimistic, where it is hindered by insufficient awareness, inherent disadvantages, and practical implementation challenges (Lahori *et al*., 2017). Although PG, as an abundant and generally low-cost industrial byproduct, has the potential to support environmental sustainability through resource recycling when appropriately treated and managed, the high cost of PG pretreatment and the complexity of the resource utilization process are obstacles to its wide application (Chen *et al*., 2025). In China, the resource utilization of PG started relatively late, resulting in the continued large-scale stockpiling of surplus material. This situation persists due to the absence of both an effective collaboration mechanism among government, industry, research institutions, and the market, and a supportive policy framework for developing the PG industry (Shi *et al*., 2024). The actual promotion is hindered by a limited distribution range and low awareness among farmers, necessitating more active guidance from the government.

Future perspectives

At the global level, PG is produced in substantial quantities, with an estimated annual output of 200–250 million tons. However, its utilization remains limited, with less than 15% being applied in sectors such as agriculture, construction, and land reclamation (Pliaka and Gaidajis, 2022). Meanwhile, BC has attracted increasing attention as a C-negative material and sustainable soil amendment. Countries including China, India, and Australia have launched pilot initiatives and C credit programs to support the deployment of BC in soil remediation and C sequestration (Singh *et al*., 2025). Nonetheless, significant disparities exist among regions in terms of regulatory policies, economic incentives, and public awareness, which hinders the widespread implementation of both materials.

Against this backdrop, the co-application of BC and PG emerges as a promising strategy to address soil degradation while valorizing industrial byproducts, particularly in phosphate-producing regions and those with significant agricultural constraints such as South Asia, North Africa, and Latin America (Singh *et al*., 2025). The combined application of BC and PG in improving and remediating agricultural soils has shown great potential, but several challenges still need to be addressed. Future research is recommended to investigate the PTEs in BC and PG and continuously optimize production conditions to reduce their heavy metal contents to within safe limits to ensure soil and crop health, as well as ecosystem sustainability. Although studies have shown that the combination of BC and PG can effectively improve soil properties, most existing research still focuses on the apparent effect. In future research, exploring the impact and mechanism of BC-PG composite on soil should be strengthened, and the optimal BC/PG ratio and application rate of BC-PG should be further explored to provide a solid theoretical basis for promoting its practical application. Most BC-PG application studies are based on laboratory, short-term, or small-scale field experiments, lacking long-term data monitoring. Thus, long-term, large-scale field experiments should be carried out to study the fate of soil amendments and track their long-term effects, which is significant to the sustainable development of agriculture. Notably, the integration of BC and PG with precision agriculture technologies, like remote sensing and geographic information systems, offers the potential to enhance the efficiency of soil amendment and remediation efforts. Additionally, the development of innovative production methods and the use of other available waste materials in combination with BC and PG may further enhance the economic and environmental sustainability.

Overall, the combined application of BC and PG in agricultural soils can produce a green synergistic effect, with promising prospects for mitigating soil degradation. However, continued research and innovation are needed to fully realize the potential of soil improvement, maximizing both environmental and economic benefits.

CONCLUSIONS

The comparative advantages and disadvantages of individual applictions of BC, PG, and their combined application from technical, environmental, and economic perspectives are summarized in Table II. Research into the combined application of BC and PG for soil improvement has increased annually. Combining these two substances can enhance soil fertility, adjust soil pH, and immobilize heavy metals, thereby improving crop production and quality. The green synergistic effects of BC and PG benefit soil health, crop productivity, and agricultural sustainability. Utilizing these low-cost industrial and farming wastes also brings significant economic benefits, and their immense potential for agricultural soil applications is increasingly evident. However, some challenges remain to be overcome, such as quality and safety control of BC and PG, cost and dosage control, and long-term impact on soil ecosystems. In the future, continuous research efforts and coordinated policy-industry development are needed to support the widespread application of BC and PG in agricultural production.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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TABLE II

Advantages and disadvantages of individual applications of biochar (BC) and phosphogypsum (PG) and their combined application (BC+PG) in agricultural soils from technical, environmental, and economic perspectives (PI, PII, and PIII, respectively)

Amendment	Advantages[a)]	Disadvantages	References
BC	PI: increasing soil aggregate stability, porosity, WHC, CEC, organic matter, N, P, K, Ca, and Mg contents, reducing soil bulk density, immobilizing heavy metals, improving soil biodiversity, PII: reducing GHG emissions, promoting C sequestration, PIII: generating potential revenue from C credits, utilizing low-cost agricultural residues as feedstock	PI: variable performance depending on feedstock and pyrolysis conditions, PII: high energy use in production, possible contamination from feedstock, PIII: high production cost for high-quality BC, limited large-scale infrastructure	Nayak *et al*., 2013; Ahmad *et al*., 2014; Minardi *et al*., 2017; Araújo *et al*., 2019; Weng *et al*., 2020; Akfas *et al*., 2024; Lin *et al*., 2025
PG	PI: suppling Ca, S, and P, improving soil aggregation, hydraulic conductivity, and WHC, ameliorating soil sodicity, PII: recycling industrial byproducts, reducing waste stockpiles, PIII: abundant and inexpensive raw material, low processing cost	PI: potential release of impurities (*e.g.*, heavy metals and radioactive elements), PII: groundwater pollution by leachate, dust emission during handling, PIII: high transportation and application costs, limited market demand in some regions	Yu *et al*., 2019; de Figueiredo *et al*., 2021; Silva *et al*., 2022; Qi *et al*., 2023; Divyangkumar and Panwar, 2024; Elbagory *et al*., 2024
BC+PG	PI: improving soil structure and nutrient availability, ameliorating soil salinity, PII: combining waste recycling with C sequestration, improving soil health while reducing environmental footprint, PIII: reducing soil amendment cost, enabling large-scale waste valorization, increasing crop yield and economic return	PI: requiring optimization for mixing ratios, heterogeneous material behavior, PII: risk of combined pollutant release if not properly managed, PIII: limited studies on economic feasibility, requiring initial investment in processing	Jalali *et al*., 2019, 2025; Peng *et al*., 2020; Guéablé *et al*., 2021; Chen *et al*., 2025

[a)] WHC = water-holding capacity; CEC = cation exchange capacity; GHG = greenhouse gas.

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