

Systematic Review

Utilization of Biochar Alone and in Combination with Compost for Removal of Potentially Toxic Metals Accumulated in Soils Associated with Land-use Patterns

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Abstract

Background: Potentially toxic metals in soils are a threat to food security and human health because it enters the food chain through crop uptake. Hence, it is critical to understand the levels of potentially toxic metals in soils due to agricultural land use patterns and the approach to remove them from the soil.

Objective: This review discussed the effect of different land-use patterns on heavy metal accumulation and their removal using biochar.

Methods: A desktop review employing preferred reporting items for systematic review and meta-analysis was used to analyse information from peer-reviewed papers including journal articles, books, thesis, and reports.

Results: It was shown that potentially toxic metals mainly found in the soil include arsenic (As), copper (Cu), cadmium (Cd), zinc (Zn), chromium (Cr), cobalt (Co), nickel (Ni), antimony (Sb), mercury, thorium (Th), lead, silicon (Si), and selenium (Se). The sources of these potentially toxic metals accumulation in soils were the application of organic and inorganic fertilizers, irrigation, use of pesticides and weedicides, and atmospheric deposition. However, different land-use patterns (greenhouse field, vegetable field soils, forest field, and maize field soil) had a significant accumulation of heavy metals (Cr, Ni, Cu, As, Cd, and Zn) due to increasing crop yield after the use of fertilizers and pesticides. Biochar was found to be effective in the removal of 18 to 40% of these potentially toxic metals from the soil. The mechanisms of removal included precipitation, physical sorption, complexation, ion exchange, and electrostatic interaction.

Conclusion: Biochar applied alone or with compost is highly stable to remove heavy metals accumulated in soils due to land use patterns.

Keywords: land use, heavy metals, potentially toxic metals removal, biochar, compost, mechanisms

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1 INTRODUCTION

Potentially toxic metals are the major principal pollutants found in the soil. Their presence in soils affect the quality and functions of soil and largely cause environmental hazard^[1-3]. The soil is a non-renewable natural resource that provides various critical ecosystem functions, including supporting the growth of crops and the distribution of water and gases in the environment. It also serves as a buffer in the control of organic and inorganic substances^[4,5]. Globally, heavy metal pollution of soil has attracted growing attention^[6]. According to He et al.^[7], about 10 million soil sites worldwide are polluted, with more than half of these pollution caused by heavy metal. The availability of heavy metals in soils is caused by multiple anthropogenic and natural factors. The toxicity of potentially toxic metals that naturally accumulate in agricultural soils in the environment is often insufficient to cause harm to human health^[8]. The principal anthropogenic sources include waste disposal, fertilizer application, long-term wastewater application in agriculture, waste incineration and traffic emission^[9,10]. The human use of land and management strategies have been implicated in the degradation of land including the introduction of heavy metals into soils^[9]. Agriculture activities, deforestation, urban development, and other human activities have significantly altered the earth's landscape^[11-13]. In developing countries, heavy metal pollution in soils has become a major environmental concern due to the changes in land-use patterns over time^[14]. Agriculture is one of the major land-use patterns leading to the contamination of heavy metals in soil, which is associated with the use of fertilizers, pesticides, and herbicides to increase crop yield^[15]. Inconsistently, it has been documented that the application of organic and inorganic fertilizers continuously increases soil pollution of heavy metals^[16], and these heavy metals contaminate the land from non-point sources when carried in runoff water^[16].

Soil pollution due to heavy metal affects soil functions negatively, reduces plant diversity and the quality of crops such as rice, and impacts the evolution of soil microbes and their linked functional genes^[17-19]. Accumulation of heavy metals in agricultural soils through various land-use patterns will cause disorder of functions of the soil, which in turn affects crop productivity. However, potentially toxic metals can be transferred to crops, thereby posing a risk to human health^[20,21]. The concentration of arsenic (As), chromium (Cr), lead (Pb), cadmium (Cd), Nickel (Ni), zinc (Zn), and copper (Cu) above the threshold level is harmful

to the health of humans^[22]. To ensure safe and healthy food production, it's critical to decrease the accessibility of heavy metals and phyto-availability to plants and to restore polluted soils^[23]. According to Hayyat et al.^[22], in situ method of remediation has been reported in studies about the remediation of soils polluted with potentially toxic metals. Biochar has been studied extensively as an in-situ soil amendment in recent years, and it contributes to removing potentially toxic metals in soils^[24,25]. Biochar is a stable solid partially combusted (pyrolyzed) and a recalcitrant compound that improves soil's physical, chemical, and biological properties and carbon (C) stock in the soil^[26,27]. Biochar is a carbonaceous sorbent usually prepared from biomass (crop residues), which is formed after specific thermochemical conversions (pyrolysis) under low oxygen (O) supply conditions^[28]. Biochar sequesters large amounts of C and has high chemical stability in contaminated soils^[22]. Biochar application has been observed to be an effective method for treating soils contaminated with potentially toxic metals, as heavy metals are absorbed through biochar application, bioavailability decreases and toxin-induced stress to plants and living organisms^[23,29]. A few studies have looked at the accumulation of potentially heavy metals in soils, but few have done a systematic review of their removal from the soil^[30-33]. Research on heavy metals accumulation and the variation in agriculture land use and other land use patterns is of theoretical and practical importance. It helps to optimize land use and prevents extreme accumulation of potentially toxic metals that leads to soil degradation and potentially entering the food chain^[34-38]. The review focused on the effect of various land-use patterns on the accumulation of potentially toxic metals or heavy metals in soils and the use of sole application of biochar in a combination of compost for the removal of potentially toxic metals.

2 METHODS

A systematic review of the literature was conducted through the examination of scientific databases and grey literature to obtain scientific evidence relevant to the objective of the study. The results are reported according to Preferred Reporting Items for Systematic Review and Meta-analysis guidance^[39].

2.1 Search Strategy

A literature search was conducted across a broad range of online databases, websites, and knowledge repositories such as Scopus, Web of Science, and Google Scholar, which allowed the identification of both peer-reviewed and grey literature. Boolean operators (AND,

and OR) were used to broaden the search in combination with keywords and synonyms such as heavy metals, heavy metal accumulation, agricultural land use pattern, accumulation of heavy metals through land use pattern, biochar for heavy metal removal, a combination of biochar and compost, mechanisms for removal of potentially toxic metals through biochar and compost. The results were screened against inclusion criteria by two independent reviewers, with additional supervision by a third investigator. The search was restricted to peer-reviewed studies published in English. References were also cross-checked and screened to be included in the study. An initial check was performed to check repeated articles. The articles obtained were further screened for inclusion and exclusion.

2.2 Inclusion Criteria

All articles involving heavy metals and land-use patterns and written in English were included in the review. Studies focused on the heavy metal accumulation, heavy metals and their accumulation in soils as a result of land use patterns, use of biochar and compost for heavy metal removal, mechanism of heavy metals removal, types of biochars and the rate of application.

2.3 Exclusion Criteria

Articles that were excluded from the research review included studies that focused on mining, soil fertility management, water pollution, and waste management, biochar application for greenhouse gas mitigation. Selected articles were also limited to those that were written in English. Other reasons for exclusion were the impossibility to retrieve the full text and the type of article (systematic reviews or opinion/position papers, guidelines, editorials, or commentary were excluded).

2.4 Selection Process and Data Extraction

The titles and abstracts were read first, followed by reading the full texts in the screening process. The screening process was carried out by all authors (Hanyabui E, Phares CA, Botchway E, Sarpong AK, Apori SO, and Manfo OP) independently and data were extracted. Disagreement was resolved through thorough discussion among the authors until a consensus was reached, and in extreme cases, a colleague with the same or similar field of study was consulted. Data were collected and recorded into a spreadsheet after the final list of suitable full-text articles was defined. The results were synthesized using a narrative synthesis.

3 RESULTS AND DISCUSSION

The literature search yielded 170 articles on Scopus, 268 on Web of Science, and 184 on Google Scholar, among which 120 were removed before screening because of duplication, acceptability, and others, remaining 502 single citations. After title and abstract

screening, 209 articles were rejected. Using inclusion and exclusion criteria, 42 articles were included in the qualitative synthesis (Figure 1).

3.1 Land Uses

Climate change, socioeconomics (culture and population dynamics), and government policy are the key determinants of land use^[40]. The use of the land would typically aim to promote social welfare, but its market value is far from being a reliable gauge of its social value, especially in developing nations where completely competitive land markets and rigorous legislative limitations of land use are infrequent^[41]. Land use changed quickly in the second half of the 20th century as a result of the implementation of agricultural and economic policies^[42]. Due to rural depopulation and the modernization of agriculture, significant changes occurred in human land use in the 20th century (second half). Plants, soil, nutrients, and water are all greatly affected by the way the land is used and managed^[15].

The ramifications of changing agricultural land use described in the literature seem to vary by regions^[43], which is supported by the fact that studies concentrate on various geographic locations^[44,45]. Land-use change usually lead to cultivating management change, which might compromise the soil quality^[46-48]. As heavy metals in soil have a direct impact on human health through food production, the level of heavy metals in soil is increasingly emerging as one of the key indicators of soil quality^[49]. Currently, researchers have focused on the consequences of land use patterns on soil heavy metal accumulation, with an emphasis on agricultural land uses, including farmland, uncovered vegetable land, orchards and forest land^[50-52]. The growing of vegetables in the greenhouse has evolved extremely rapidly in recent years and greatly aided in the supply of agricultural products, particularly vegetables, which is one of the significant land-use patterns in China. Some agricultural practices, such as the excessive and incorrect application of chemical and organic fertilizers, have caused the soil quality in greenhouse vegetable fields to deteriorate and decline^[49].

3.2 Potentially Toxic Metals or Heavy Metals

There have been numerous debates over the definition of the term “heavy metals”^[53]. Heavy metals were proposed by some researchers based on their high atomic weight, while others on the basis of density, chemical characteristics, toxicity, or density. However, the term “heavy metal” has recently been applied to metallic chemical substances and metalloids that impact the environment negatively and humans^[54-56]. Heavy metals, according to Banfalvi^[57], are naturally occurring elements with a high atomic weight and a density five times greater than that of water. Examples of heavy

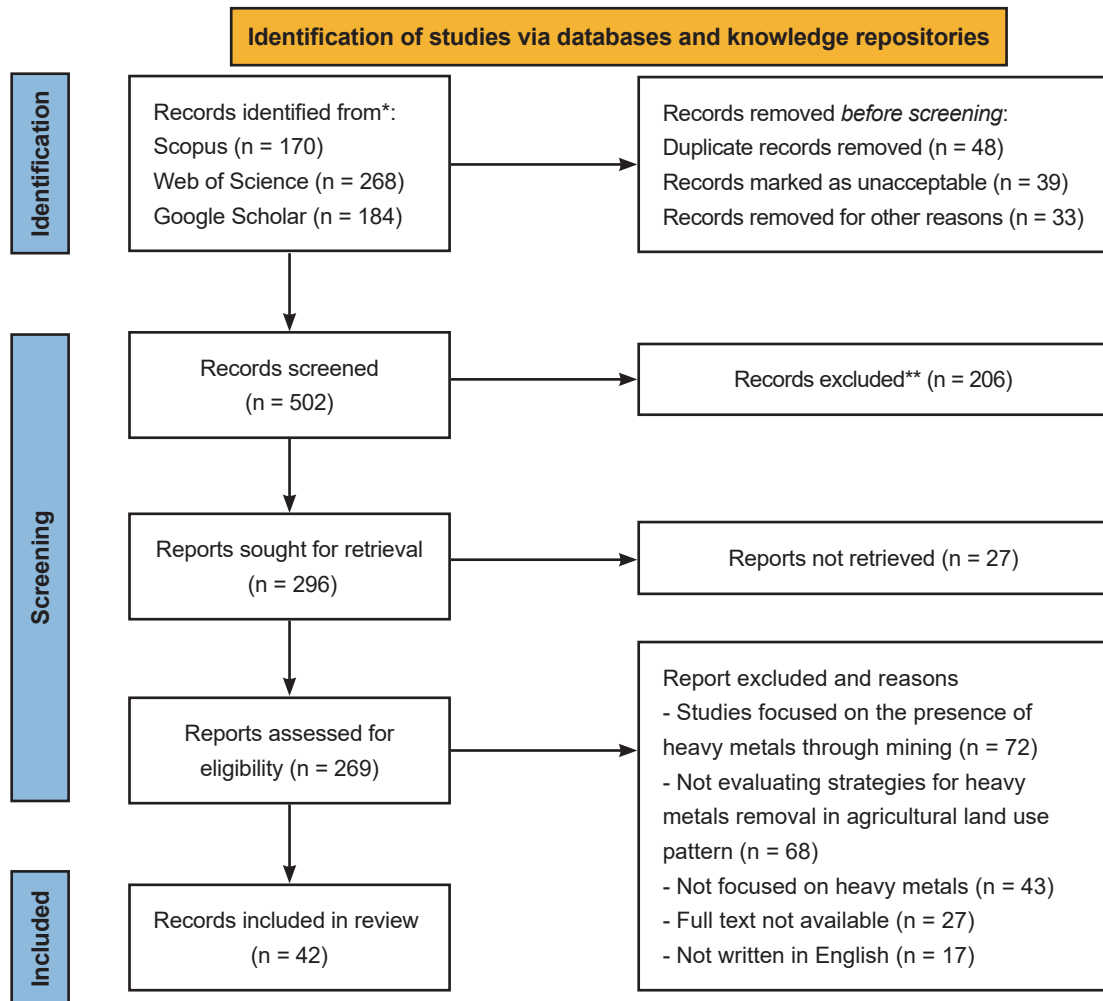


Figure 1. Flow chart of article selection process. Source: <https://www.bmj.com/content/372/bmj.n71>

metals that are seen in our everyday life are titanium of atomic number 22, vanadium (atomic number 23), Cr (atomic number 24), manganese (atomic number 25), iron (atomic number 26), Co (atomic number 27), Ni (atomic number 28), Cu (atomic number 29) Zn (atomic number 30), As, molybdenum, silver, Cd, tin, platinum, gold, mercury (Hg) and Pb^[54-56]. Potentially toxic metals, such as aluminium, Se, and As accumulate in the human body, cause damage to the soft tissues, and also become hazardous to the environment^[58]. Metalloids also called trace elements such as Zn and molybdenum, are not hazardous or harmful to the environment, and they are referred to as microelements because of their limited activities in the soil^[53].

3.3 Potentially Toxic Metal Sources in Soil

Sources of potentially toxic metals in the soil can be expressed as follows^[59].

$$M_{total} = (M_p + M_a + M_f + M_{ag} + M_{ow} + M_{ip}) - (M_{cr} + M_l)$$

Where;

M is the potentially toxic metal; p is the parent material; a is the atmospheric deposition; f is the source

of fertilizers; ag is the source of agrochemicals; ow are the sources of organic waste; ip are other inorganic pollutants; cr is crop removal; l is the losses by leaching, volatilization, etc.

Naturally, potentially toxic metals occur in the soil ecosystem from the weathering phase of the parent material and are regarded as trace (<1,000mg kg⁻¹) and hardly toxic^[60]. Cd has been reported to occur naturally in the soil at a concentration ranging between 0.1-1mg kg⁻¹ and is mostly found in sedimentary rocks^[61]. Enhanced concentrations of As are estimated from shales, clays and phosphates-bearing minerals, while Cr is found in all rocks but high concentrations are reported in mafic and ultramafic rocks^[62]. Some of the natural sources of heavy metals are volcanoes, rock disintegration and soil erosion.

Anthropogenic sources of heavy metals in the soil are more mobile and thus more bioavailable than pedogenic heavy metals^[63,64]. Potentially toxic metals linked to human activity, including leaded gasoline and Pb-based paints, fertilizer application, animal manure application, biosolids (sewage sludge), compost, pesticides, coal

combustion residues, petrochemicals, and atmospheric deposition are partial sources of accumulation in the soil. Other sources include high metal waste disposal in unregulated landfills, leaded gasoline, Pb-based paints, and biosolids^[65-67]. Heavy metals such as Cd, Cr, Hg, As, and Pb are associated with human activities. Anthropogenic activities that contribute to heavy metals include incomplete fossil burning, mineral extraction, landfilling, metal refining, electronic goods manufacturing, dyes, agricultural chemicals, military operations and vehicular emissions^[68].

3.4 Distribution of Potentially Toxic Metals in Soil

Li et al.^[69] studied the distribution and relationship with soil characteristics of the top 70 heavy metals under various land use and found that potentially toxic metals are distributed in soils depending on land use patterns, especially agriculture land use. Other related research has shown that potentially toxic metals in soil exhibit heterogeneous distribution in the vertical and horizontal directions in different ecosystems^[70,71]. Ye et al.^[72] suggested that the distribution of heavy metals in the soil near a river was high and decreased with the increase of distance from the river. Diane et al.^[73] compared the distribution of elemental Pb in the riparian and agricultural land use in southern Canada and found that the concentrations of Pb in the soil of the riparian area were almost 12 times that of those in the agricultural area. Young et al.^[74] carried out descriptive statistics for the heavy metal distribution in the agricultural soils of Taiyuan and concluded that out of seven metals, only Ni was normally distributed.

Potentially toxic metals are evenly distributed at the depth of 20cm of the soil profile and most of them extended down between a soil depth of 20 to 40cm, indicating highly varying characteristics nature of the soil profile^[75]. Atafar et al.^[76] stated that Pb distribution was in the range of 1.6-6.05mg kg⁻¹ soil before fertilization and reached the range of 2.75-12.85 after harvesting, an increase by 2 folds. The distribution of the Mn, Zn, Cu, Ni, Co, Cr, Pb and Cd in soil profiles, and surface soils was investigated. It was shown that the soil-forming processes resulted in a separation of these elements between various soil components, causing differences in the distribution patterns. He concluded that the ionic radius is of major significance for such distribution^[77].

3.4.1 Agricultural Land Use and Accumulation of Potentially Toxic Metals

Numerous studies have revealed that the massive accumulation of potentially toxic metals in agricultural soils has contaminated the food chain and become a serious problem for human and livestock consumption despite the wide variances in the distribution of heavy metals in soils^[76-79]. The accumulation of heavy metals

mostly occurs in surface soils and may result in deleterious effects on most plant species without any detectable effect on groundwater quality^[80]. Cd and Pb are the two types of heavy metals that accumulate more readily in surface soils but significantly decrease in the lower horizons^[81]. Recent studies in agricultural soils have indicated that potentially toxic metal accumulation has exceeded its thresholds^[82-86]. Organic and inorganic fertilizer applications containing heavy metals are the main sources of potentially toxic metal accumulation in those soils. In addition, the application of pesticide-containing heavy metals, such as mancozeb, has been implicated to contribute substantially to heavy metal accumulation in the soils^[49]. The variations in the concentration of the heavy metals could be attributed to the different rates of fertilizer application under different land-use patterns. Trace metals are essential nutrients but are required in small quantities. The deficiency of trace elements (Cu, Co, Fe, Mn, Mo, Ni and Zn) negatively affects the growth of plants^[87]. The concentration of trace metals could be increased in deficient soils and improve crop yield using inorganic fertilizers^[87]. Wuana et al.^[88] posited that Cu deficient soils for cereal production are occasionally treated with Cu whilst Mn is supplied to root crops. Additionally, farmers apply large amounts of fertilizers to the soil in intensive farming systems to provide adequate N, P, and K for crop growth^[88]. Heavy metals such as Cd and Pb are present in the compounds used to produce these elements at minor levels. Their levels in the soil may be much higher due to the continuous application of fertilizers^[89]. Wuana et al.^[88] reported that most weedicides used in agriculture productivity and horticulture contain substantial concentrations of heavy metals. The chemicals used to formulate the pesticides contain Cu, Hg, Mn, Pb, or Zn. Therefore, continuous application of pesticides, weedicides, fungicides, and insecticides in various fields results in the accumulation of heavy metals. Cu accumulation in the soil is mainly attributed to agricultural activities such as the continuous application of Cu-based fungicides and pesticides^[90]. Application of biosolids such as manures, compost, and municipal sewage sludge to the soil inadvertently leads to heavy metal accumulation^[88], though they serve as an organic amendment for soil fertility improvement.

Globally, twenty million hectares of cultivable land are irrigated with wastewater. According to studies, wastewater irrigation-based agriculture provides 50% of the urban areas' supply of vegetables in some Asian and African towns^[91]. In general, farmers are more concerned with increasing their yields and earnings than with environmental advantages or risks. Despite the typically low levels of heavy metals in wastewater effluents, irrigation of the land for an extended period with wastewater can eventually lead to heavy metal buildup

in the soil^[88]. Different land-use patterns (greenhouse field, vegetable field soils, forest field, and maize field soil) have a significant difference in the accumulation of potentially toxic metals of As, Cr, Ni, Cu, Cd, and Zn but did not show any effect on the accumulation of Pb^[49]. When heavy metal accumulation exceeds the standard, soil contamination occurs and negatively affects the sustainable development of the ecological environment and social economy^[31,92]. Huang and Jin^[93] concluded in their work that the accumulation of heavy metals in soils is significantly affected by land use, especially in agricultural lands.

Barman et al.^[94] observed that the transfer of potentially toxic metals in the soil to part of a plant did not follow any trend and varied with the type of heavy metal, species and plant parts. Again, Barman et al.^[94] observed in their studies that out of 32 plant samples analyzed, the percentage of the sample showing metal accumulation ratio (soil to other parts of the plant) ≥ 1 is as follows in descending order; Fe (84.0%)>Cu (81.3%)>Ni (59.3%)>Cr (46.9%)>Zn (31.3%)>Pb (17.4%)>Cd (9.4%). The ratio >1 indicates a very high accumulation in the plant tissues than in soil.

3.5 Types of Biochar

3.5.1 Agricultural and Forestry Waste Biochar

Waste generated from agricultural activities and forestry can be used to produce biochar. This type of biochar has gained popularity in the area of pollution control due to its low cost and ease of acquisition^[95]. Biochar made from agricultural wastes such as seed shells^[96], corn cob^[97], corn straw^[98], and potassium-iron rice straw^[98] could effectively remove Cu²⁺ and Pb²⁺ ions from the soil, with removal capacities of 1.67, 2.08, and 0.41mmol/kg, respectively.

3.5.2 Wood Biochar

Studies have demonstrated that natural wood and waste wood are essential and common resources used to produce biochar. Some trees can survive all year round and can grow well even in hard situations, representing a plentiful source of the material. Recently, eucalyptus^[99] and mulberry^[100] have been used to prepare biochar, and biochar made from these materials are considered effective adsorbents for removing harmful chemicals from contaminated soil^[101]. When utilizing biochar made from eucalyptus and pine, rates of Cu and Pb removal from the soil were 93% and 90%, respectively^[102,103].

3.5.3 Industrial Waste Biochar

Industrial organic waste, such as sludge^[104], and municipal solid trash comprise the majority of industrial waste^[105]. From 2010 to 2019, research on biochar production from industrial waste increased by 70%. Biochar produced from industrial waste at a temperature

of 750°C was observed as an efficient adsorbent for Cu²⁺ removal, with a maximum adsorption capacity of 18.5mg/g^[106].

3.6 Characteristics of Biochar

Numerous studies have used the initial biomass feedstock and its biochar to illustrate the basic physicochemical properties of both raw and pyrolyzed content^[107,108]. Zhang et al.^[95] reported that biochar from feedstocks varies greatly in chemical characteristics due to the type of feedstock. The fundamental elements of biochar are C, hydrogen (H), O, S, and nitrogen (N). It is also known that biochar contains fixed C, which is used to estimate the amount of carbonaceous compounds present in the biochar solids. Van Krevelen's diagrams demonstrated the inconsistency of using the H/C and O/C ratios to calculate aromaticity and maturity degrees^[108]. Basic O-H, O-C, and C-H ratios have been established to determine the degree of pyrolysis and the amount of biochar oxidative modification in soil and solution systems^[109,110]. However, it has also been shown that biochar contains functional groups such as carboxylic acids, lactic acids and phenols. Due to the presence of tube fractures that were initially created by plant cells, biochar produced at various pyrolytic temperatures has a characteristic shape resembling honeycombs. Brunauer, Emmett, and Teller are widely distributed in biochar as a result of these well-developed pores^[111,112]. Applied biochar produced at a low pyrolysis temperature in combination with inorganic fertilizer is considered suitable as it regulates nutrient release^[111,112]. Additionally, biochar prepared at low temperatures is much more stable than biochar prepared at high temperatures. Once integrated into the soil, however, the porous structure becomes unstable and the fine fractions are abraded^[108].

3.6.1 Biochar for Removing Heavy Metals Accumulated in the Soil

Heavy metals and their concentration can be removed from the soil following biochar application. Biochar is a stable material, mostly carbonaceous, produced from pyrolysis and gasification of biomass^[113]. Due to the polar functional groups, large surface area and transition metals of biochar, it can absorb heavy metals through a variety of adsorption processes^[95,113]. When it comes to heavy metal removal in soil, biochar is non-selective and is therefore beneficial for heavy metals accumulated in soils due to land use patterns^[114]. The biomass used to produce the biochar, pyrolysis temperature and the method of production has a major impact on the biochar properties^[113,114]. As, Cu, Cd, Zn, Cr, Co, Ni, Sb, Hg, Th, Pb, Si, and Se are the potentially toxic metals that can be found in the soil^[113]. Their accumulation in the soil can be toxic to human and plant life. To produce biochar that can be used to remove heavy metals from the soil,

the type of biomass and reactivity should be taken into consideration^[115]. Also, the physical properties of biochar will change if the temperature during the pyrolysis is increased^[113,116]. When the pyrolysis temperature is increased between 400°C to 900°C, the biochar surface area also increases from 0.1 to 3.2-100-500m²/g^[117]. The unique characteristic of biochar (ion exchange and sieve-like nature) is the ability to absorb and trap heavy metals accumulated in soils^[113].

The application of biochar for heavy metals removal can be done in three different ways, including functional group complexation, the release of cations, and physical adsorption or surface precipitation^[116]. For functional group complexation, heavy metals react with the hydroxyl functionalities on the biochar surface^[116]. A metal cation such as Ca²⁺ or Mg²⁺, which may be present in the structure of the biochar, exchanges heavy metals like Pb²⁺ for the process of ion exchange^[116]. The amorphous nature of biochar traps heavy metals during the physical adsorption or surface precipitation process^[116]. Biochar applied, which is pyrolyzed at a temperature of 900°C, can decrease Cu, Zn, As, Pb, Cd, and Cr from 91.65 to 9.44wt%, 98.82 to 63.34wt%, 97.91 to 52.11wt%, 55.91 to 4.87wt%, and 73.51 to 9.57wt%, respectively^[116,118]. When the pyrolysis temperature of biochar increases, its adsorption capability gets better. This is because biochar pyrolyzed at higher temperatures has a higher concentration of functional groups that contain O on their surface^[116]. Results from an experiment conducted by Liang et al.^[119] using rice husk biochar produced at a temperature of 500°C to remove heavy metals accumulated in wetland surrounding soil showed that biochar could remove or reduce heavy metals. because the reason is that the concentration of heavy metals such as Cd, Cu and Zn reduced from 5.59 to 4.73mg kg⁻¹, 53.9 to 51.57mg kg⁻¹, and 210.82 to 194.59mg kg⁻¹, respectively. Hu et al.^[116] reported that as a result of a large number of polar functional groups in biochar, such as carboxyl, hydroxyl, and carboxyl groups, the heavy metal ions, was adsorbate by physical sorption and complexation mechanisms. They added that the immobilization of heavy metals in the soil by biochar was also improved by ion exchange, precipitation, and the trapping of the potentially toxic metals in the nanopores of the material. Application of biochar can effectively reduce bio-availability of Pb, Zn, Ni, Cd, and Cu^[120].

Different materials used to produce biochar cannot have the same efficiency to remove heavy metals from the soil, which may be attributable to the different structures and stability produced by biochar produced. This is consistent with the study conducted by Wang et al.^[71] where biochar applied reduced heavy metals (Cd, Cr, Hg, and Pb) accumulated in the soil considerably. They used biochar produced from pig manure and corn straw, and it

was noticed that the concentration of Hg (0.79mg/kg) was reduced by pig manure biochar to 0.34mg/kg and corn straw biochar to 0.59mg/kg. Biochar produced from pig manure was observed to remove more heavy metals from the soil systems due to its higher surface area (surface area for corn straw and pig manure biochar samples was 10.7 and 26.8m²/g, respectively)^[116].

3.6.2 Mechanisms of Biochar for Heavy Metal Removal in Soil

Immobilization of heavy metal activities in the soil is achieved through the exchange adsorption of biochar surfaces. The higher the cation exchange, the heavier metals are retained^[109,121]. Ion exchange occurs when positive modifications in the soil and negative charge groups on the biochar surface contact electrostatically^[122]. This type of reaction falls under nonspecific adsorption and is reversible due to its lower adsorption energy. The cationic function is determined according to the way the biochar is aromatised^[122]. The ability to lose electrons from functional groups increases and the impact of adsorption becomes more substantial as their conjugate aromatic structure is present to a larger extent^[123]. According to Wang et al.^[122], adsorption and dissolution-precipitation of mineral constituents in biochar could effectively reduce heavy metal activity. Soil pH can increase through biochar application and the reaction of heavy metal ions with -OH, PO₄³⁻, and CO₃²⁻ can form hydroxide, carbonate or phosphate precipitation, effectively increasing heavy metal concentrations^[121,122]. Biochar complexation is important for the fixing of heavy metal ions with high affinity^[122]. Studies indicated that the reactions of oxygenic functional groups such as hydroxyl group (-OH), carboxyl group (-COOH) and amino group (-NH₂) with heavy metals on the surface of biochar contribute significantly to the adsorption of heavy metal ions^[123,124]. Biochar applied can absorb heavy metal contaminants more effectively and remove them from the soil because of their larger surface area and increased surface energy^[122]. Many factors influence the effect of the adsorption of biochar on heavy metal ions, including biochar source materials, pyrolysis temperature, soil pH, physical and chemical properties of heavy metal ions, and the biochar application rate^[122]. Under identical conditions, despite the biggest surface area, biochar produced from animal manure outperforms sludge biochar and plant biochar in terms of heavy metal ion adsorption. This is because P-rich biochar from animal feces can precipitate or coprecipitate with particular heavy metal ions, making the biggest contributions to the healing process.

3.7 Characteristics of Compost

One of the most efficient ways to benefit from organic waste is by converting it into useful amendments such as compost for soil fertility improvement^[125]. Due to the growing demand for ecologically friendly methods of

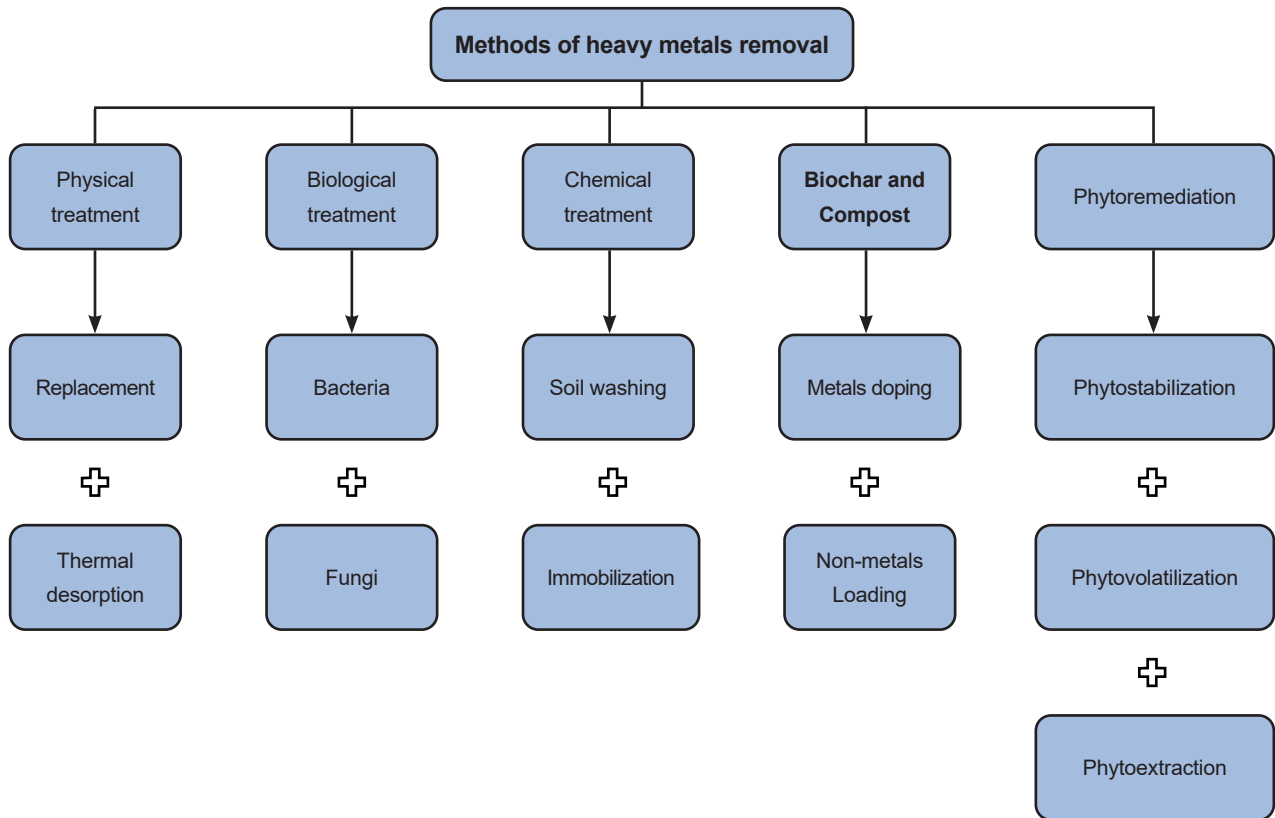


Figure 2. A flowchart showing different methods used for heavy metal removal accumulated in the soil. Source: <https://linkinghub.elsevier.com/retrieve/pii/S209549561830901X>

treating waste and organic agriculture products, interest in composting has recently surged^[125]. Composting is a more effective technique of waste disposal that enables the recycling of organic matter, without mentioning that it is environmentally friendly to dispose of waste^[126]. The utilization of compost prepared from manure has captured great attention recently. The management of the composting process depends on the succession of mesophilic and thermophilic microorganisms, both of which are active in the process^[127]. The quality of composts made from various organic wastes varies, and depending on the composition of raw material and the composting process utilized^[128]. The quality of compost is mostly dependent on its stability and maturity. Compost maturity and stability are related to phytotoxicity and the activities of microorganisms. Morel et al.^[129] reported that the population of microorganisms, monitoring biochemical properties of microbial activity and biodegradable ingredients analysis are biological activities of compost, which can be used to determine the compost's maturity.

3.7.1 Compost Application for Heavy Metal Removal

The presence of humic substances, mineral ions, and microorganisms in compost can decrease the risk of heavy metals' ecological and environmental effects and their immobilization in soils for agricultural productivity^[130,131]. Composting may facilitate to lower the risk of agricultural

failure, financial losses, and heavy metal exposure dangers to people. Compost is considered a fantastic waste management choice worldwide. Following the composting process, organic wastes lose most pathogens and parasites, lose weight and have their phytotoxicity from heavy metals and organic contaminants discharged^[132,133]. In agriculture, compost has been used as an alternative to synthetic fertilizers. Evidence indicated that the use of compost improved the soil's physical characteristics and fertility, enhanced microbial activity and crop biomass, and enhanced crop development^[134-136]. To reduce or eliminate heavy metals that built up in the soil through agricultural land use, composting is a cheap, extremely useful, and environmentally beneficial method.

The majority of research found that the addition of compost to soils can reduce or immobilize heavy metals in agricultural soil by altering the physical and chemical properties of the soil and reacting with the heavy metals^[137,138]. The majority of research found that adding compost to soils can immobilize or reduce heavy metals in agricultural soils by altering the physical and chemical properties of the soil and interacting with the heavy metals^[139,140]. However, the risk associated with applying compost in agriculture cannot be overlooked. Irfan et al.^[141] found that the application of compost at the rate of 0.5, 1, 2, and 4% to artificially contaminated soil reduced the concentrations of Pb, Cd, and Cr, respectively. The

Table 1. Removal of Potentially Toxic Metals in Soil with Different Biochar Types and Their Mechanisms

Ref.	Biochar Type	Heavy Metals	Matrix	Adsorption Mechanism
Lu et al. ^[159]	Sludge biochar	Pb ²⁺	Soil	Complex reaction with hydroxyl (-OH) and carboxyl (-COOH) Precipitation and complexation
Cao and Harris ^[160]	Dairy manure	Pb ²⁺	Soil	Ion exchange, adsorption, and precipitation with PO ₄ ³⁻ , CO ₃ ²⁻
Liang et al. ^[161]	Dairy manure, rice straw	Pb ²⁺	Soil	Electrostatic adsorption, ion exchange
Xie et al. ^[162]	Walnut green husk	Pb ²⁺	Soil	As a result of the aromatic structure, it reacts with the heavy metal and ion exchange with functional containing O groups
Liu et al. ^[163]	peanut shell, Chinese medicine residue	Pb ²⁺	Soil	Complexation, ion exchange, electrostatic adsorption, and pH increase make the Pb ²⁺ -carbonate bounded state to changed into Pb ²⁺ insoluble phosphate and silicate state
Kong et al. ^[164]	Beanpoles	Hg ²⁺	Soil	Precipitation, forming Hg (OH) ₂ , HgCl ₂
Dong et al. ^[165]	Brazilian pepper	Hg ²⁺	Soil	A composite reaction with hydroxyl (-OH) and carboxyl (-COOH) reacts with an aromatic structure to form Hg-π
Xu ^[166]	Sugarcane, walnut wood chips	Hg ²⁺	Soil	Composite reaction with hydroxyl (-OH) and carboxyl (-COOH), ion exchange, electrostatic adsorption
Zhao ^[167]	Rice husk and rice straws	Hg ²⁺	Soil	Composite reaction with hydroxyl (-OH) and carboxyl (-COOH), ion exchange
Ippolito et al. ^[168]	Broiler litter	Cu ²⁺	Soil	Complexation with functional groups to form Cu ₃ (CO ₃) ₂ (OH) ₂ , CuO
Mohan et al. ^[169]	Oak biochar	Cr (VI)	Soil	Deoxidize Cr (VI) into Cr (VIII) complex reaction with hydroxyl (-OH) and carboxyl (-COOH)
Yang et al. ^[74]	Sugarcane leaves, tapioca stem, rice straw, silkworm excrement	Cd ²⁺	Soil	Electrostatic adsorption precipitate with CO ₃ ²⁻ , OH ⁻
Zhang ^[146]	Maize straw	Cd ²⁺	Soil	Electrostatic adsorption, precipitation)
Guan et al. ^[170]	Pine needle, maize straw, dairy manure	As ⁵⁺	Soil	Electrostatic adsorption
Huang et al. ^[171]	Maize straw	As ³⁺	Soil	Non-electrostatic physical reversible adsorption and chemical irreversible adsorption with polar groups
Wang et al. ^[172]	Hardwood	As ³⁻	Soil	Increase the solubility of As ³⁻
Wu et al. ^[173]	Almond Putamina, reed straw	Ni ²⁺	Soil	Composite reaction with hydroxyl (-OH) and carboxyl (-COOH)
Wang et al. ^[71] Chen et al. ^[174]	Water hyacinth Hardwood	Zn ²⁺	Soil	Electrostatic adsorption and ion exchange
Xu ^[166]	Dairy manure	Pb ²⁺ , Cu ²⁺ , Zn ²⁺ , Cd ²⁺	Soil	Oxygenic functional groups and precipitate with PO ₄ ³⁻ , CO ₃ ²⁻
Xu ^[166]	Rice husk	Pb ²⁺ , Cu ²⁺ , Zn ²⁺ , Cd ²⁺	Soil	Phenolic hydroxy group with surface complex with

level of lead decreased from 18.26 to 7.13mg k/g when 4% of compost was applied. Also, the concentration of Cd in soil was decreased from 9.33mg k/g to 5.36mg k/g at a 4% rate of compost application, and the Cr content was reduced at 4% compost application from 18.47mg k/g to 7.34mg k/g. The higher (amount) the compost application rate, the more the remediate or reduction of heavy metals^[141]. The different methods used for removal of heavy metals accumulated in soil are presented in Figure 2.

3.7.2 Mechanism of Compost for Heavy Metal Removal in Soil

The application of compost serves as a bio sorbent to absorb potentially toxic metals^[142,143], and the composting capacity of adsorption capacity can be assessed using kinetics of adsorption and experiment involved with

adsorption isotherms^[144-146]. Simantiraki and Gidarakos^[147] reported that compost has a better removal capacity than zeolite and is reported to reduce or remediate the availability of heavy metals in water through chemical adsorption by 85-89%. The availability of potentially toxic metals in soil can be remediated using compost by altering the physicochemical characteristics (such as pH, oxidation-reduction potential, and organic matter content of soils. This will also help soil particles to more effectively bind with potentially toxic metals^[148,149]. Predominantly, the application of compost immobilizes potentially toxic metals through the inorganic component, substance of humus, and microorganisms^[150-152]. They further explained that the large number of organic functional groups (carboxyl, carbonyl, and phenols) is ascribed to the abundance of humus in the compost which binds metal ions through complexation.

Table 2. Removal of Potentially Toxic Metals in Soil With Different Types of Compost and Their Mechanisms

Feedstock type	Heavy Metals	Effect	Effective Mechanisms	Ref.
Municipal organic waste (MOW) and Domestic organic waste	Zn, Cu, Ni, Pb, Cd	Compost produced from DOM and MOW can absorb heavy metals	Process of adsorption	Venegas et al. ^[175]
Municipal solid waste	Cu, Cd, Pb, Ni, Zn, Cr	No significant influence on mobility factor of metals	Both soluble and insoluble complexes were formed with organic compounds	Achiba et al. ^[176]
Green waste	Cu, As Pb	Mobility and solubility of As and other metals were increased	Organic C and Fe in soil pore water were enhanced	Clemente et al. ^[177]
Animal manure and Green waste	As, Cu	Was able to reduce the mobility and leachability of Cu but not As	Surface complexation	Tsang et al. ^[178]
Market waste	As	As levels in soil pore water were improved	Availability of phosphorous improved and increase in water-soluble Fe and C in pore water	Hartley et al. ^[179,180]

Table 3. Combined Application of Biochar and Compost for Potentially Toxic Metals Removal in Soil and Their Mechanisms

Combinations	Heavy Metals	Mechanisms	Ref.
Biochar + Compost	Cu, Pb	The high P and Fe content in the compost and biochar increased the soil organic matter content, soil pH	Karami et al. ^[181]
Biochar + Compost	Zn, Cd, Cu, Pb	Free ions form a complex with organic ligands and heavy metals exchange with Ca ²⁺ , Mg ²⁺ , and other cation associated	Zeng et al. ^[182]
Biochar + Compost	Cu, Ni, Pb, Zn	The pH of the soil increase and stable compounds between organic materials and heavy metals are formed.	Rodríguez-Vila et al. ^[183,184]
Biochar + Compost	As, Zn, Cd, Cu	Soil pH increases and dissolved organic C affects soluble phosphorous on As	Beesley et al. ^[185]
Biochar + Compost	Pb, Cd, Cu, Zn, As	Soil pH increases, dissolved organic C, and soluble phosphorous	Beesley et al. ^[186]

Furthermore, compost shows diverse affinities to different potentially toxic metals. According to Chien et al.^[153], the linkage of humic substances with potentially toxic metals followed an increasing order: Pb>Cu>Cd>Zn. Because of the composition of humic (hydrophilic and hydrophobic compounds), it can act as surfactants^[133].

Applied compost can immobilize potentially toxic metals through biosorption and biomineralization due to the availability of microorganisms in the compost^[154,155]. Some isolated microbes (*Penicillium chrysogenum*, *Graphiumputredinis*, *Fusarium solani*) that are present during the composting process is able to absorb more than 90% of lead in the soil^[156]. The presence of manganese, iron and aluminium in the compost can retain heavy metals regularly^[157,158].

Removal of potentially toxic metals in soil with different biochar types and their mechanisms are presented in Table 1^[159-174].

The removal of potentially toxic metals in soils using different types of compost and their mechanisms are showed in Table 2^[175-180].

The application of biochar and compost together for the removal of potentially toxic metals in soils and their mechanisms are presented in Table 3^[181-186].

3.8 Biochar and Compost

The synergy between biochar and compost has the efficiency to remove heavy metals accumulated in soils^[187]. An experiment conducted by Tang et al.^[187] applied biochar (rice straw biochar at a pyrolysis temperature of 500°C) and compost (compost produced from rice straw, vegetable leaves, etc) at the same rate and showed that integration of biochar and compost, sole application of compost, and sole application of biochar reduced Cd by 87.1%, 69.6% and 65.8% respectively. Hu and Gholizadeh^[116] reported that through electrostatic interactions and chelation processes, the high surface area and high amount of polar functional groups in biochar could immobilize the heavy metals. Due to the presence of humic substances, composting leads to improved stabilisation of heavy metal organometallic compounds.

4 CONCLUSION

The present review reveals that the accumulation of

potentially toxic metals in agricultural soils is significant and has exceeded thresholds. This is associated with various agricultural land use patterns which are currently practiced. It was noticed that heavy metal accumulation through agricultural land uses is associated with the application of chemical and organic fertilizers, pesticides and herbicides by farmers to increase crop yield. Applying pesticides-containing heavy metals, such as mancozeb, is implicated to contribute substantially to heavy metal accumulation in the soils. Chemicals used to formulate the pesticides contain Mn, Cu, Hg, Pb, or Zn. Therefore, the continuous application of weedicides, pesticides, fungicides, and insecticides, in various fields leads to the accumulation of heavy metals in soils. As heavy metals are accumulated in the soil, biochar and compost application are available to remove the accumulated heavy metals. Biochar has a high surface area and includes abundant polar functional groups and transition metals, which can easily absorb potentially toxic metals through different adsorption mechanisms. The complexation, cationic and physical adsorption of biochar's functional groups allows for the potential removal of accumulated heavy metals. Considering the compost, its application can remediate potentially toxic metals in agricultural soils by changing the physical and chemical properties of soils and reacting with potentially toxic metals. Sometimes compost applications also introduce some potentially toxic metals into the soil. But the synergy between the biochar and compost helps to immobilize the heavy metals accumulated. The high levels of polar functional groups in biochar can immobilise potentially toxic metals through electrostatic interactions and chelation mechanisms, and the humus in the compost also enhances the stable organometallic complexes of potentially toxic metals.

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Conflicts of Interest

The authors declared no conflict of interest.

Author Contribution

All the authors contributed to the conceptualization and methodology; Hanyabui E, Phares CA and Botchway E contributed to the definition of the search strategy, article screening, data extraction; all the authors contributed to original draft preparation, review and editing. The manuscript was read by all the authors and agreed to be published.

Abbreviation List

As, Arsenic
C, Carbon
Cd, Cadmium
Co, Cobalt

Cr, Chromium
Cu, Copper
H, Hydrogen
Hg, Mercury
N, Nitrogen
Ni, Nickel
O, Oxygen
Pb, Lead
Sb, Antimony
Se, Selenium
Si, Silicon
Th, Thorium
Zn, Zinc

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