REVIEW



Use of Additives in Composting Promotes Passivation and Reduction in Bioavailability of Heavy Metals (HMs) in Compost

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Abstract

Composting influences heavy metal (HM) speciation by transforming the exchangeable and reducible forms of HMs to oxidisable and residual forms, promoting the redistribution of HMs to a more stable form thereby reducing their mobility, leachability, and bioavailability. This enhances HM passivation hence reducing environmental contamination and possible HM-related toxicity. In this review, we explored the impact of additives/ameliorants on HM passivation during composting and the reduction in HM bioavailability in compost. Using additives in composting improved the passivation of HMs and reduced the bioavailability through several mechanisms. Additives may not reduce total HM concentration but reduce the bioavailable concentration, which is of importance in risk assessment. However, vermicomposting is exceptional, as it reduces total HM concentration. Improving humification and microbial activity is at the heart of HM passivation in composting. Overall, conditions and substances that promote humification, thermophilic phase, and improve microbial community structure enhance HM passivation in compost. Combining suitable composting additives depending on HMs of interest and vermicomposting the final compost is most likely to yield the best result in reducing HM bioavailability cum total concentration to achieve a safe final product.

Introduction

Heavy metals (HMs) are described as elements with high density compared to water (Tchounwou et al. 2012). Based on the hypothesis that toxicity and heaviness are inter-connected, HMs also include metalloids like arsenic that can trigger toxicity at low-level exposure (Duffus 2000). There has been increasing public health and ecological concern connected to environmental pollution of HMs. Human exposure to HMs has increased significantly due to the exponential increase in the utilisation of HMs in numerous industries, agriculture, technology, and domestic activities (He et al. 2005; Tchounwou et al. 2012). Even though HMs are

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naturally occurring elements that are abundant in the environment, most human exposure and environmental contamination occur due to anthropogenic activities such as smelting operations and mining, industrial use and production, and agricultural and domestic use of metals and their derivatives (Tchounwou et al. 2012). Also, heavy metal (HM) contamination in the environment can occur through atmospheric deposition, leaching, metal corrosion, and evaporation.

Hitherto, HMs contamination is still a global environmental quagmire, which signifies a potential threat to plants, animals, and humans because of its non-degradable nature (Chen et al. 2015). Majority of HMs are highly soluble in water, thus readily accumulate in the ecosystem and transfer into the food web (Wei et al. 2020). HMs accumulate in organic solid wastes like sewage sludge, municipal solid waste, animal manure, and other biowastes (Wei et al. 2015; Wang et al. 2019a, b, c; Zhu et al. 2019) and this poses a significant threat to the ecosystem. For example, in agricultural systems, prolonged application of animal manures may provoke enormous HM accumulation in agricultural soils, presenting potential public health risks through crop food consumption (Lin et al. 2021). Taking into consideration the possible presence of HMs in organic waste residues and animal manure (Chen et al. 2020a, b, c), the elimination of HMs



during composting is to a great extent the most significant direct strategy to resolve their environmental impact (Chen et al. 2020a, b, c).

Composting is a multifaceted biological process, which depends on the interaction of different microbial communities to convert organic wastes into stable, safe, and nutrientrich organic fertiliser (Li et al. 2019a, b, c). The composting process can be completed under anaerobic or aerobic circumstances. Under aerobic composting, organic substances are decomposed in the presence of oxygen. Numerous studies have established that aerobic composting decreases the mobility and possible bioavailability of HMs by enhancing HM complexation (Awasthi et al. 2019; Chen et al. 2019a, b). HMs are redistributed during composting and the speciation favours oxidisable and residual forms that are more stable and less available compared to the exchangeable and reducible forms in manure/waste feedstock that are mobile, unstable, and more bioavailable. Improving humification is the primary mechanism of HM passivation in composting. Figure 1 shows improved humification as a common effect of composting additives that are effective in reducing HM bioavailability in the final compost.

Nonetheless, caution is still very much applied regarding the expansion of compost application in the agriculture sector, because of the likelihood of severe side effects like HM accumulation in the soils (Achiba et al. 2009; Carbonell et al. 2011). Even though HM bioavailability could potentially be moderated during composting (Zhou et al. 2018; Cui et al. 2020), Wang et al. (2016) reported high bioavailability of HMs in traditional composting. This could be attributed to processing conditions that have been established to influence HM bioavailability (Chen et al. 2020a, b, c). Hence,

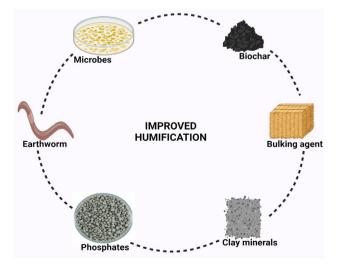


Fig. 1 Improved humification is the primary mechanism of effective composting additives in reducing HM bioavailability

suppressing the bioavailability of HMs during composting is vital in maintaining the safety of the products.

The passivation of HMs during compositing is predominantly shown in the reduction of the mobility and bioavailability of HMs, which is heavily reliant on the specific chemical speciation in the metals rather than the total concentration (Hao et al. 2019). The degree of bioavailability of HMs and their mobility in compost products have a significant effect on their projected accumulation and release into plants and soils. Meanwhile, Achiba et al. (2009) reported that compost application increased the total concentration of HMs in soil, but these HMs were in their residual and oxidisable fractions. Chen et al. (2020a, b, c) in their review, identified microbes as the main actors in reducing HM toxicity in compost. However, other researches have consistently shown the presence of high concentrations of HMs fractions in soils after composting, which could lead to secondary pollution of the soil by HMs and potentially limit their cyclic utilisation (Chen et al. 2019a, b). This pitfall necessitated the introduction of additives during composting.

The addition of additives during composting is a suitable strategy that helps to decrease the form distribution of contaminants in the environment and accelerate the composting process. The introduction of composting additives can reduce the bioavailable fractions of HMs or alter their redox status, hence decreasing the mobility of HMs and their bioavailability in compost products (Derakhshan Nejad et al. 2017). Among all the diverse additives employed during composting, such as phosphogypsum, oxalic acid, superphosphate, clay, zeolites, and biochar are famous with unique characteristics for efficient diminution of HMs bioavailability and mobility (Barthod et al. 2018; Shan et al. 2021; Liu et al. 2022a, b, c). This is because of their active free valences, maximum internal surface area, and optimal particle sizes (Barthod et al. 2018). In addition, these additives possess high exchange capacity for cation as well as functional groups that contain oxygen in the surface area that are relatively conducive for HM retention. These attributes make them resourceful and efficient adsorbents for HMs binding (Ozdemir et al. 2020). Figure 2 shows the level of improved HM passivation achieved by adding bulking agent and applying other additives (biological, chemical, mineral, and organic) in composting when compared to composting without additives.

Additives like phosphate rock, lime, graphene oxide, medical stone, zeolite, and biochar have been predominantly applied to stimulate the stability of HMs and promote the safety and quality of the product during composting (Khan et al. 2009; Singh and Kalamdhad 2014; Liu et al. 2017; Yang et al. 2019; Wei et al. 2020; Wu et al. 2021; Chen et al. 2021a, b, c, d). These findings suggest that when additives were introduced during composting, the final product was safe and more stable when compared to those produced



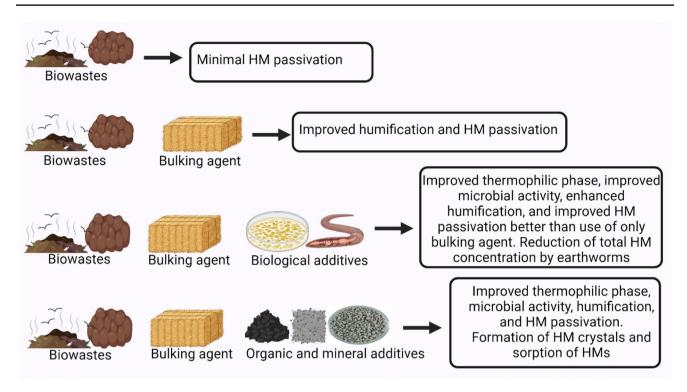


Fig. 2 Benefits of bioavailability reduction using bulking agents and additives in composting

through conventional composting. However, considering the varied nature of additives, mechanisms, methods, and characteristics, it has been difficult to establish the optimum amount of additive required to enhance the reduction of bioavailability of HMs during composting. Simultaneously, a few reviews have been conducted to explore the impact and bioavailability of HMs (Smith 2009) as well as their remediation strategies, mechanism of toxicity, and speciation (Chen et al. 2020a, b, c) during composting. Hitherto, previous reviews have not provided holistic information about the influence of additives on the reduction of HM bioavailability during composting. Therefore, this review was carried out to explore the impact of additives/ameliorants on HMs passivation during composting and the reduction in HMs bioavailability in compost.

Mechanisms of HMs Passivation in Compost

Improved Humification

Organic matter (OM) degradation/mineralisation by microbes and nematodes is the basic mechanism for HM passivation in compost. Microbial degradative activity is the primary driving force behind successful composting. For composting to be successful, the right feedstocks are required under a suitable C:N ratio (20–30), moisture (50–70%; and 65–85% for vermicomposting), and porosity.

Humification changes OM structure and functional groups aiding the formation of organo-metal complexes through the complexation of HMs with humic substances (HS) (de Souza et al. 2019; Song et al. 2021). Microbes can break down lignocellulose compounds into fatty acids that could bind HMs (Cui et al. 2020).

Humification influences the physicochemical properties during composting, which in turn contributes to the redistribution and speciation of HMs. HMs are less mobile at high or alkaline pH; therefore, the high pH of compost promotes HM passivation and transformation to residual fractions (Vandecasteele et al. 2013; Shen et al. 2016; Guo et al. 2022). Total phosphorus (TP) correlates positively with the passivation of some HMs (Pb, Zn, Cd) (Guo et al. 2022; Xu et al. 2022), total potassium (TK) correlates positively with Pb passivation (Xu et al. 2022), humic acid (HA) correlates positively with HMs (Cu, Cd, Zn, and Pb) passivation (Achiba et al. 2009; Li et al. 2021a, b; Pinto et al. 2020), and other HS showed a relationship with HM passivation (Zhang et al. 2018; Cao et al. 2022). The impact of fulvic acid (FA), humus, and OM is higher on some HMs (Cu, Zn, Cd, and Pb) (Achiba et al. 2009; Pinto et al. 2020; Li et al. 2019a, b, c). CEC improves biochar sorption of HMs and influences HM speciation through electrostatic interaction (Jain et al. 2019; Liu et al. 2017). Phosphate improves the transformation of HMs (mainly Zn, Cu, and Pb) to stable compounds. FA, high in compost feedstocks, is converted into a more stable HA with active functional groups (hydroxyl, phenolic



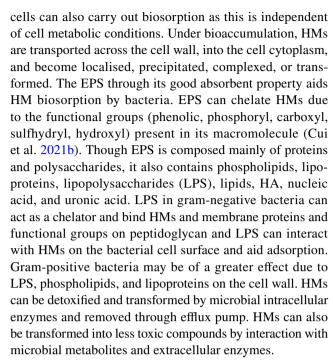
hydroxyl, hydroxyl quinone, carboxyl, quinone) that aids HM adsorption and complexation (Kulikowska and Gusiatin 2019). C:N ratio reduction in combination with decomposition of OM leads to HM passivation. OM is negatively charged and can bind positively charged metal ions. Temperature is a key factor in compost humification as the high temperature at the thermophilic phase promotes microbial activity, hence enhancing humification and HM passivation.

Thermophilic Phase

The thermophilic phase of composting is important as it affects microbial activity thereby affecting humification. High N content and low C content negatively affect the thermophilic phase. High C content and poor porosity delay the onset of thermophilic phase, hence adequate C:N ratio and porosity are important at the beginning of composting (Wu et al. 2017). These suitable conditions are achieved by adding the right quantity of bulking agents. Thermophilic peak temperature, thermophilic phase duration, and how long it took to attain thermophilic phase are important contributors to composting success and compost quality. This is because it controls the removal of pathogenic microbes, composting duration, compost maturity, microbial activity, and microbial community structure. HM leaching is high at high temperatures and reduction in total HM concentration at the end of composting has been attributed to leaching for Cd, Pb, Ni, and Cr (Vandecasteele et al. 2013; Xu et al. 2022). The high rate of microbial activity at this phase leads to high microbial metabolites and enzymatic actions that could lead to direct or indirect interaction with HM ions leading to reduction or formation of compounds of varying stability. Microbes and microbial products could sequester, immobilise, inactivate, complex, chelate, adsorb/absorb, and precipitate HMs through exopolymeric substance (EPS) formation, metabolites production, enzymatic actions, efflux pump, and cell wall interactions.

Microbes and Earthworms

Microbes are responsible for OM degradation in composting. In the absence of microbial activity, humification and composting will be unsuccessful. Microbes through their activities, properties, and genetic repertoire can sorb, transform, or reduce metals hence reducing their bioavailability and ecotoxicity. The bacterial cell wall is negatively charged, which could promote binding to positively charged metal ions through electrostatic effects (Guo et al. 2022). Biosorption is possible through HM interaction with bacterial cell walls leading to sorption, which could be through adsorption, chelation, ion exchange, complexation, precipitation, and bioaccumulation. These are dependent on the properties of the bacterial cell wall and its environment. Hence, dead



Bioreduction of HMs to less toxic forms is possible through direct action with bacteria enzymes (e.g. reductase), or indirect interaction with reducing metabolites. Microbes can biomineralise HMs by converting HM ions to stable minerals like Fe–Mn oxides, phosphates, and carbonates. Compost increases the amount of Zn associated with Fe–Mn oxides (Achiba et al. 2009). Earthworms can accumulate HMs in their gut and intestines and transform them through enzymatic activities, hence leading to passivation and reduced HM contamination (Swati and Hait 2017). Earthworms can improve composting humification and microbial activity, hence enhancing HM passivation. Earthworms can also reduce the total contents of HMs in compost due to their high HM accumulation ability.

Organic and Mineral Additives

Clay minerals and biochar can sorb HMs due to their structural properties. HMs can sorb to pores in these additives or bind to functional groups (hydroxyl, alcohol, carboxylic) on the surface of biochar. The O-containing groups on biochar can form complexes and precipitates with HM ions. These additives also promote humification, thermophilic phase, and microbial community structure. Hence, they also provide the benefits from those factors. Biochar has an alkaline pH, which affects the pH of the composting process, leading to increased pH and negative charge, hence aiding electrostatic interactions between HMs and negative charge, thereby causing HM passivation. The alkaline pH of biochar could be attributed to its calcium, potassium, phosphate, and magnesium content that can also interact with some HMs leading to inactivation (Jain et al. 2019). The large surface



area of biochar and certain clay minerals, provide a suitable habitat for microbial attachment aiding biofilm formation through quorum sensing and EPS production, which in turn enhances HM inactivation (Chen et al. 2020a, b, c). Phosphate additives can react with HMs forming stable complex compounds and precipitates. They also promote humification and improve microbial activities, thereby enhancing the benefits of these factors. Figure 3 shows the impacts of additives on composting properties and HM passivation.

Influence of Composting on HMs Speciation and Reduction

The presence of HMs in sewage sludge and municipal solid wastes is a major challenge in their utilisation as a soil conditioner. Composting (and composting conditions) of biosolids can help passivate the HMs and reduce their leachability, mobility, and bioavailability hence making them permissible for agricultural purposes. For instance, thermophilic conditions (40–120 °C) favour the growth and multiplication of most thermophiles responsible for improving the binding of HMs to stable HA during sewage sludge composting (Kulikowska and Gusiatin 2019). This implies

that thermophilic composting could promote passivation and reduction in the bioavailability of HMs in compost. HMs bind majorly with FA in compost feedstocks before composting and redistribute to more stable HA during composting hence promoting HMs stability.

Composting wastes and animal manure can passivate/ immobilise HMs and reduce their bioavailability of HMs (Chen et al. 2021a, b, c, d; Meng et al. 2017). The total concentration of HMs increases in composting with time, as the breakdown of OM continues with gaseous emissions and evaporation of moisture (Chu et al. 2021). However, the bioavailable HMs concentration (which is of more importance in HMs risk assessment) is reduced through redistribution, inactivation, passivation, and immobilisation during composting. Aeration rate, initial moisture content, and composting duration were identified as the main factors affecting the reduction of Cu and Pb bioavailability in pig manure composting (Shen et al. 2016). The reduction in exchangeable Cu and Pb positively correlated with increased pH. The optimum conditions were given as 0.1 m³ min⁻¹ m⁻³ for aeration rate, 20 days for composting duration, and 65% for initial moisture content. The composting duration was 50 days, hence increased duration is unlikely to increase HM passivation in composting.

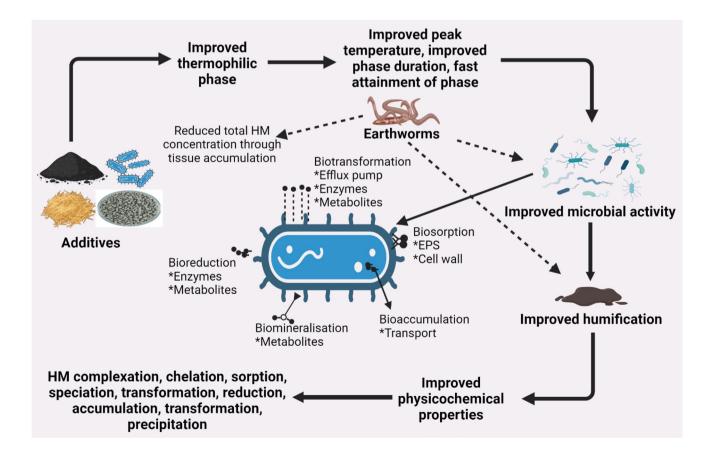


Fig. 3 Impact of composting additives on composting properties and HM passivation

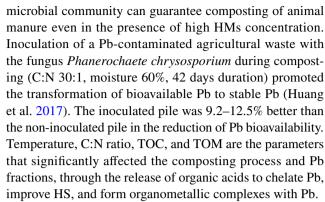


Aerobic composting of pig manure with maggot and chicken manure inactivated HMs (Pb, Zn, Cu, Cr, and Cd) in the final compost (Xu et al. 2021). Maggot manure was good in HMs inactivation and the transformation of FA to HA was high in maggot manure, thereby signifying the importance of HA/FA in HMs inactivation. The aromaticity of the compost increased through reduction in compounds containing aliphatic groups, and moisture content was identified as an important factor in metal inactivation. The risk of HMs in waste is not exclusive to biosolids and animal manure. A study identified Cd as the major HM of concern in food waste probably due to the presence of plastics in food waste (Chu et al. 2019). The severity of the HMs hazards follows the sequence Cd>Cr>Pb>Hg>As.

Composting poultry litter increased the total concentration of HMs (Cu, Zn, Cr, and Pb) and the transformation of labile peptides, carbohydrates, and fatty acids into more stable forms (de Souza et al. 2019). This led to a decrease in aliphaticity and polarity and an increase in the aromaticity and hydrophobicity of the organic materials. Hence, composting stabilises OM and mineral components of waste. These structural changes consequently reduce HMs solubility because the humified organic fractions of HMs tend to increase. Composting had a significant effect on the immobilisation of HMs and metalloids in animal manure (Shehata et al. 2021). Composting reduces the bioavailability of HMs irrespective of feedstock, but this is dependent on the HM, composting process, and some physicochemical parameters (pH, OM, P, N) (Vandecasteele et al. 2013). This impact will most likely be effective on HMs with better affinity for HS and P (e.g. Cu, Zn, Cd, and Pb), and those passivated at high pH.

Impact of Microbial Inoculation

Inoculating beneficial microorganisms in composting can help improve humification and HM passivation. Bacteria have a negatively charged cell wall that could directly bind positively charged HM ions through electrostatic adsorption (Guo et al. 2022). Microbes could affect the functional groups and composition of OM through humification hence indirectly aiding complexation with HM (Song et al. 2021). Also, microbes could break down ligneous bulking agents into fatty acids that could bind HMs at varying stabilities (Cui et al. 2020). Microorganisms can easily adapt to HMs in composting and subsequently improve the composting process as was observed during chicken manure composting (Chen et al. 2022a, b, c, d). This is possible by synergistic cooperation among the microbes through shared responsibility, as different bacterial groups carry out varying functions to help the microbial community adapt to HMs. This synergism is achieved through quorum sensing. Hence,



Industrial composting (60% moisture, 70 days duration) of livestock manure using domestic sludge, furfural, straw, and biochar–straw combination immobilised various HMs (Zn, Cu, Cr, As, Pb, Cd, Ni, and Mn) at varying extents, and the addition of microbial inoculum (*Bacillus* strains) enhanced the reduction in the bioavailability of Cu and Cr (Cao et al. 2022). This was through improved OM degradation and formation of HS, which in turn binds metal ions. *Phanerochaete chrysosporium* inoculation in sewage sludge composting improved HMs (Ni, Cu, Zn, and Pb) stabilisation through improving OM transformation and promotion of humus formation (Zhang et al. 2018).

Microbes do play a role in the availability of HMs in compost. The bacterial phyla Firmicutes and Proteobacteria were identified to control the phytoavailability of Pb and Cr, whereas Actinobacteria, Bacteroidetes, and Proteobacteria controlled the phytoavailability of Zn and Cu in municipal sludge composting (Tang et al. 2019). Therefore, microbial community structure plays a significant role in HMs passivation in composting. The microbial phyla Proteobacteria, Firmicutes, Bacteroidota, and Chytridiomycota were reported as dominant in composting by Guo et al. (2022). Firmicutes, Proteobacteria, Bacteroidetes, and Actinobacteria were the major phyla for HMs immobilisation in cow and pig manure composting (Shehata et al. 2021). This shows that, though HMs are non-biodegradable, they can be converted into a stable form, thereby reducing their bioavailability and possible risk of toxicity.

Composting of cow manure and tree litter with or without inoculation of beneficial microbes reduced the solubility of Pb, Cu, and Zn (Pinto et al. 2020). Inoculation with beneficial microbes reduced the bioavailability of Zn and Cu through binding to stable HA, though the total concentration of all the HMs was not suitable for agricultural application. Microbial inoculation proved to be better than noninoculated composting (65% moisture; 25:1 C:N; 30 days duration) for HMs reduction, but inoculation alone is not sufficient to reduce the HMs content to acceptable limits. Therefore, vermicomposting the compost or the addition of other composting additives is required under microbial inoculation to achieve enhanced passivation. Inoculation of



pig manure composting with effective microbes (photosynthetic bacteria, Bacillus spp., Lactobacillus spp., Actinomycetes spp., yeast spp.) at 0.5% was effective in reducing the ecotoxicity of pig manure, and significantly reduced the bioavailability of Pb and Cu, which correlated with varying microbial community structure (Zhou et al. 2020a, b). The study outlined the relationship of speciation of different HMs with varying fungal and bacterial species. The inactivation rate was 46.99% and 60.79% for Cu and Pb, respectively, with an increase in residual fraction at 56.63%, 26.39%, 75.92%, and 17.88% for Cu, Zn, Pb, and Cd, respectively. Despite having some microbial genera/species attributed to the reduction in bioavailability of certain HMs in composting, the impact of microbial activity on specific HMs is entirely different under different composting feedstocks (Chen et al. 2019a, b). The relative abundance of the microbial species is a determinant factor in their influence on HM bioavailability (Guo et al. 2022). This implies that despite the presence of a given microbial species if the relative abundance is low, it may not have a significant influence on the bioavailability of HMs. Microorganisms can become adaptive to HMs during composting, and HMs were found to show toxicity to microbes in the order Cu > Zn > Cd (X. M. Chen et al. 2020a, b, c). This adaptation to HMs contamination can be utilised in HMs remediation, and in contrast, can become a challenge concerning the spread of heavy metalresistant bacteria (HMRB).

A combination of HMRB from compost and humin (from the maturity phase of composting) was examined for biosorption of HMs (Cu, Zn, Pb, Ni, Cr, and Cd) in composting (C:N 30:1; 50-60% moisture; 50 days duration) (Wei et al. 2020). Humin could bind HMs but HMRB from composting had better metal binding ability than humin, and a combination of both markedly enhanced HMs removal. Microbial biomass and humification of humin are two synergistic factors responsible for HMs biosorption. A combination of HMRB and humin was recommended for improving HMs removal in composting. This is in line with the positive impacts of microbial adaptation to HMs contamination. It could be possible that the mechanisms through which bacteria resist and adapt to HMs may be influential in reducing HM bioavailability by HMRB. In that case, processes like biosorption, metal efflux, quorum sensing, biofilm, and EPS formation could influence HMs immobilisation, sequestration, and precipitation in composting.

A consortium of bacteria (*Acinetobacter pittii*, *Bacillus subtilis* subsp. *stercoris*, and *Bacillus altitudinis*) at 1% v/w in swine manure (swine manure:corn stalk; 6:1 w/w) composting improved humification and residual fractions of HMs (Cr, Cd, and Pb) better than control (Li et al. 2021a, b). The HA showed a positive correlation with the HMs residual fractions. The microbial inoculation passivated Cr and reduced the amount of exchangeable Cd but did not affect

exchangeable Pb. The inoculation of bacteria also strengthened the propagation of Firmicutes, Proteobacteria, and Actinobacteria. Hyperthermophilic composting (dewatered sludge:corn stalk; 3:2 dry wt) using *Ureibacillus terrenus* at 5% rate (dry wt) enhanced reduction in HMs bioavailability better than control (Qin et al. 2022). It increased the residual proportion of Cu and Pb by 6.3% and 15.3%, respectively, when compared to the control. Inoculation of *Thermus thermophilus* in sludge composting promoted the biotransformation of Pb(II) to a more stable chloropyromorphite form thereby reducing its bioavailability (Chen et al. 2021a, b, c, d). The passivation of Pb occurred through selective accumulation by biosorption and became transformed through biomineralisation.

Structural equation models showed that physicochemical properties and bacteria community influence HMs bioavailability in beet cattle and chicken manure composting (60% moisture; 20:1 C:N; 40 days) (Chen et al. 2019a, b). Temperature, OM, pH, and moisture were important parameters for reducing HMs bioavailability in chicken manure composting, while OM and temperature were the critical physicochemical factors for beef cattle manure. The bioavailable content of Cd decreased at the thermophilic phase, which could be that Cd is sensitive to temperature, or through improved microbial activity in response to adapting to the high temperature leading to the release of metabolites. This could lead to the formation of EPS through quorum sensing, which could in turn sequester HMs and reduce possible bioavailability. Binding to OM could increase the residual fraction of HMs, and OM degradation enhances the production of HS and binding of HMs to HS. High pH can reduce HMs mobility and could promote precipitation of HM ions and HMs passivation. High pH was reported as the likely cause of the reduction in bioavailable Cd by Vandecasteele et al. (2013). After ageing a 40-day animal manure compost to 50–365 days, Chen et al. (2019a, b) concluded that there is no likely benefit in the reduction of HM bioavailability by composting for a long period. This is corroborated by an earlier report by Shen et al. (2016) that 20 days was the optimum composting duration for HMs (Cu and Pb) passivation during a 50-day composting period.

Effects of Bulking Agents and C:N Ratio on HMs in Composting

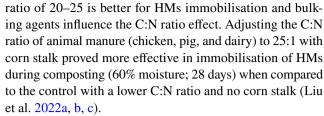
Bulking agents are mainly plant materials used in composting to improve porosity and get the starting C:N ratio to the desired value (around 20–30). The effectiveness of bulking agents in composting is manifested in increased nutritive value, fast degradation of materials, improved moisture, suitable pH, and aeration in composting. Studies by Chang and Chen (2010) revealed that bulking agents like rice husk,



sawdust, and rice bran increased the degradations of composts and churned out a very good quality compost from food waste. A high C/N ratio (above 40) can lead to prolonged composting duration and a low C:N ratio (below 15) enhance nitrogen loss through gaseous emissions. Equally, if the C:N ratio is high, nitrogen presence will be diminished, and bacteria present in the compost cannot compete with fungi to utilise the carbon. Therefore, the compost heap may fail to produce the temperature necessary to produce good compost. The C:N ratio can be regulated by selecting the most suitable combination of composting feedstocks and adding bulking agents to ensure a final ratio within the optimum range (Christos et al. 2017).

C:N ratio is an important factor in controlling the morphological transformation of HMs by affecting the microbial community structure. Influence of C:N ratio and bulking agent on HMs immobilisation and bacterial diversity was reported in swine manure composting. A C:N ratio of 20:1 and vinasse (bulking agent) was better than other C:N ratio (15:1 and 25:1) and other bulking agents (wheat straw and green waste) in improving bacterial diversity and HMs immobilisation (Guo et al. 2022). Metal-binding proteins, oxidase/reductase enzyme, OM (humus), electrical conductivity (EC), pH, and total phosphorus TP were influential in HMs immobilisation. Zn and Cu were potentially passivated by metal binding proteins, Zn could form a complex with humus, and As and Cr were affected by oxidase/reductase enzymes. Improved humification (OM degradation) and rise in TP and pH favours HMs (Zn, Pb, Cu, and Cd) precipitation, complexation, and adsorption. This in accordance showed the influence of microbes and environmental factors on HMs immobilisation in composting. It could also be one of the factors aiding HMs passivation under phosphate additives.

Similarly, a C:N ratio of 22:1 was better than 15:1 and 27:1 (swine manure and rice straw; 55–60% moisture, 59 days duration) for redistribution of HMs (Zn and Cu) and P fractions, and their transformation from mobile to stable form (Wang et al. 2019a, b, c). OM was also identified as an important factor in the redistribution of the HMs and P fractions. In addition, C:N ratio of 25:1 was better than 15:1 and 20:1 for reducing the mobility of Cu and Zn, and maize straw as bulking agent improved OM degradation better than rice straw (Wu et al. 2017). The impact of the bulking agent is negligible when compared to C:N ratio. This could be because of the similarity of both bulking agents. The C:N ratio affects microbial enzymes, which in turn affects metal ions in composting (70% moisture, 59 days). High N content and low C content negatively affect urease activity and thermophilic phase. A 12.6 C:N ratio could not attain thermophilic phase and a C:N ratio of 15 took longer time to reach thermophilic phase than 20 and 25 in pig manure composting (Wu et al. 2017). These reports show that C:N



On the contrary, Sidelko et al. stated that reduction in C:N ratio in sewage sludge composting (sewage sludge, straw, wood chip, mature compost inoculum) below 15:1 favours the transformation of HMs (Ni, Zn, and Cu) into stable non-bioavailable forms (Sidelko et al. 2021). In their study, reducing the straw fraction from 4:1 to 8:1 increased the non-bioavailable form of Zn, Cu, and Ni to 21–30%. The inoculation of mature compost could introduce beneficial microbes, which may have aided HM passivation. Nevertheless, it is clear from both assertions that a high C:N ratio at ≥ 35 may not favour HMs passivation and immobilisation in composting. This is because that at higher C:N ratio, there will be limited nitrogen, and nitrogen is necessary for microbial proliferation. This will potentially reduce the rate of decomposition and humification, and consequently slow down passivation.

Ligneous bulking agents (wood sawdust and maize straw) were better than inorganic additive (calcium carbonate) for improving humification and formation of HA during pig manure composting (Li et al. 2019a, b, c). The binding capacity of HA to Cu and Cd under sawdust and maize straw was better than that from inorganic agent. This suggests that the improvement in the complexation effect of compost HA is affected by the composting bulking agent. This makes the use of ligneous bulking agents necessary even under the application of other additives. Composting municipal sewage sludge with different bulking agents reduced the total concentration of Ni, Zn, and Fe when compared to compost without bulking agents (Saffari et al. 2020b). This is due to the high biomass-to-HM ratio when compared to the biomass of the pile with no bulking agent. Consequently, the mobility factor and availability of Ni and Fe were reduced. The use of cornstalk in swine manure composting reduced the bioavailability of Cr, Cu, Pb, and Cd by 54.3%, 49.2%, 26.6%, and 5%, respectively (Liu et al. 2022a, b, c).

The leachability of HMs (Cd, Cr, Pb, Ni, Mn, Cu, Fe, Zn, and Hg) decreased, and the total concentration of each HM increased during composting of paper mill sludge with cow dung, bamboo chips, and sawdust using rotary drum (Hazarika et al. 2017). The increase in total concentration of the HMs is due to a reduced volume/size of biomass, which occurred through OM decomposition during the composting process. Similarly, the total concentration of HMs in feedstock was lower than that in compost with or without bulking agents (Saffari et al. 2020a). The concentration in the compost without a bulking agent was



highest due to a decrease in the mass of sewage sludge during composting. Composting without bulking agent reduced the mobility factor of As, Cr, and Pb but that with bulking agent was significantly better. The availability of the three metals was reduced by improving stabilisation and immobilisation. All bulking agents (wheat straw, tree leaves, pistachio hull) affected HMs mobility factor and availability differently and none was preferred over the other. In addition, the different fractions of dissolved organic matter (DOM) were found to affect the distribution of HMs during food waste and sugarcane leaves composting (Shan et al. 2019). The HA, FA, hydrophilic, and hydrophobic neutrals fractions of DOM were involved in HMs redistribution during the thermophilic phase while hydrophilic and hydrophobic neutrals contained more HMs in the final compost. Pig manure composting with sawdust (4:1 fresh wt) reduced the bioavailability of Cu and Zn (Meng et al. 2017). Composting of Ageratum conyzoides with sawdust and cow dung also showed the effect of composting (rotary drum) on the leachability of various HMs (Maturi et al. 2021). Cd and Ni bioavailability was reduced to a non-detectable limit at the end of composting. The bioavailability of Fe, Mn, Ni, Cd, and Pb was reduced. The leachability of the HMs (Pb, Cr, Fe, Mn, Cu, and Zn) was moderate throughout the composting process. In general, the total HM content of the final compost was high when compared to feedstock, but the bioavailable HM content was reasonably low.

Co-composting of solid waste (sewage sludge, corn stalk, and kitchen waste) reduced the HMs contents to a safe standard for agricultural purposes (Xu et al. 2022). The process had a 45.7% inactivation rate on As but did poorly on the inactivation rate of other HMs (Ni, Pb, Cr, Cu, HG, Zn), but the HM fractions tilted towards oxidisable and residual fractions during composting. The transformation of the HMs to a more stable oxidisable and residual form is a positive effect towards a reduction in bioavailability. The percentage reduction in bioavailability was As (70.2–95.9%), Hg (31.3%), Cr (59.2–71.1%), Pb (60–76.9%), Cu (34.2–43.8%), Ni (36.6–47.3%), and Zn (39.5–48.2%). The total concentration of Cr and Ni was reduced by 71.3% and 33.4%, and this could be attributed to the loss of soluble metal ions through leachate. The pH and temperature were identified as the main contributory environmental factors and HMRB were also identified. This is corroborated by an earlier report by Vandecasteele et al. (2013) that a reduction in the total concentration of Zn and Cd in their study could be attributed to leaching during composting. Overall, composting with bulking agents improves the process and reduces HM bioavailability.

Vermicomposting on HMs Bioavailability and Total Concentration

Earthworms in association with microbes can reduce HMs mobility by enhancing microbial enzyme activities through processes in earthworm gut and cast. The reduction in total HMs concentration in vermicompost is attributed to the accumulation and immobilisation of HMs in earthworm tissues (Swati and Hait 2017). Vermicomposting can improve OM degradation, formation of HS, and stabilisation of HMs through enhanced humification and promotion of the formation of HA–HMs complexes (Wang et al. 2022). These processes explain how vermicomposting markedly reduced the bioavailability and total concentration of HMs (Cd, Cr, and Pb) in cow dung (Wang et al. 2017).

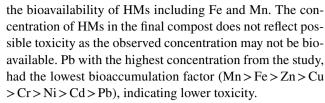
Exchangeable and reducible fractions of HMs were converted to oxidisable and residual fractions during vermicomposting (0.5kg sewage sludge per pot, 40 adult worms per pot, 65-80% moisture, 45 days) of sewage sludge, with different plant litters as bulking agents (Wu et al. 2018). The addition of these bulking agents enhanced the formation of oxidisable HMs fraction and improved its accumulation in the earthworm, hence buttressing the influence of bulking agents on HMs in composting/vermicomposting. Cd content was reduced by 31% in the final vermicompost under Bauhinia purpurea as a bulking agent. Composting sewage sludge with additives (sawdust, fly ash, straw, and soil) and vermicomposting (200 g sludge, 1.6 kg worms/m²) the composted sludge with Eisenia fetida was beneficial in sequestering HMs (He et al. 2016). The additives improved composting by stabilising the compost and reducing toxicity. The total concentration of the HMs (As, Cd, Fe, Cu, Cr, Pb, Ni, Mn, and Zn) after vermicomposting was low when compared to the final value in the control, and the initial value in the amended compost. The HMs were reduced by decreasing the HMs mobility through increasing the HMs residual fraction. According to He et al. (2016), residual form of HMs increased through the formation of organo-metal substances, essential metals (Zn and Cu) were regulated within worm tissues and excreted, while non-essential metals (Cr and Pb) were displaced by calcium (Ca) hence reducing their soluble fraction.

Information in literature has shown that vermicomposting with *Eisenia fetida* can significantly reduce HMs and improve NPK availability in biosolids (Azgin 2021; Chakraborty et al. 2022). Similarly, vermicomposting (0.6kg waste mixture, 40 worms, 65% moisture, 35 days) with *Eisenia andrei* led to significant percentage removal of HMs in sewage sludge (Rorat et al. 2017). The HMs accumulated in the earthworm, and the



HMs body accumulation factor was given in the order Cd>Cu>Zn>Ni>Cr>Pb. Analogous research reported vermicomposting (1kg feedstock—cow dung and banana leaf, 20 adult worms, 60-80% moisture, 105 days) using Eisenia fetida to reduce HMs concentration in final vermicompost with pH, TOC, and C:N ratio as critical parameters (Mago et al. 2021). The use of Eisenia fetida and Eisenia andrei for vermicomposting (40 worms-20 worms from each specie, 60% moisture) of sewage sludge reduced the concentration of HMs (Cd, Zn, Cu, Ni, and Pb) (Rorat et al. 2016). The HMs bioaccumulation factor was given in the order Cd > Zn > Cu > Ni > Pb with Eisenia Andrei showing higher accumulation ability to certain HMs. Both species showed a high inclination to accumulate Cd and Zn. Eudrilus eugeniae in municipal solid waste vermicomposting (0.624kg worms, 75-85% moisture, 70 days) reduced the concentration of HMs (Cd, Cu, Ni, Co, Zn, and Cr) when compared to composting, but not that of Fe and Mn (Soobhany et al. 2015). The failure to reduce the concentration of Fe and Mn was attributed to the mode of formation of the organic bound complexes and the accumulation efficiency of Eudrilus eugeniae, and not an increase due to OM degradation and biomass reduction. This suggests that the accumulation efficiency of earthworm to a given HM may depend on the specie of earthworm as Eisenia fetida was reported by Suthar (2008) to reduce the concentration of Fe and Mn in vermicomposting of distillery sludge. The vermicompost had a better reduction in HMs concentration than compost (an increase in total HMs concentration) and the bioconcentration factor was in the order Cd > Ni > Cu > Co > Cr > Zn.

Eisenia fetida vermicomposting showed superiority to composting (90 kg waste mixture, 3kg worm @ 1.5kg/ m2 worm density, 120 days, 70-80% moisture) in humification and reduction of HMs availability through bioaccumulation and humus-related passivation (Song et al. 2014). The concentration of the HMs was reduced at 43.3-73.5%, 11.3-52.8%, 18.9-62.5%, 21.4-47.6%, 34.6%, and 19.9-49.6% for Cd, Cr, Cu, Co, Zn, and Ni, respectively. Kaushik and Garg (2003) observed a reduction in the total content of Cr (0–25%), Fe (3.1–12.3%), and Zn (11.5–38.2%) in the final product during vermicomposting (E. fetida) of textile mill sludge mixed with cow dung. In a 77-day vermicomposting of textile mill sludge mixed with cow dung, Garg and Kaushik (2005) observed a significant reduction in total metal content at 13.8–67.3%, 26.9–41.1%, 20.8–58.1%, 0.97–41.3%, 42.7–72.4%, and 20.9–33.1% for Fe, Cu, Cd, Cr, Pb, and Zn, respectively. Similarly, Dominiguez-Crespo et al. (2012) reported a significant decrease in the content of Cu (51.3–91.1%), Ni (86.2–100%), and Zn (56.5–79.2%) after vermicomposting (E. fetida) of sewage sludge and cow dung for a period of 90 days. According to Singh and Kalamdhad (2013) vermicomposting with E. fetida can reduce



The use of 10% biochar and Eisenia fetida in composting of sewage sludge and kitchen waste (SS:KW 70:30) led to a significant reduction in HMs (Cr, Cd, Cu, Zn, Mn, and Pb) concentration (Khan et al. 2019). The body accumulation factor of the earthworm to the HMs was in the order Cd > Zn > Pb > Cu > Mn > Cr at the final phase of vermicomposting. Incorporation of phosphate rock or biochar in vermicomposting was beneficial for improving biodegradation, earthworm fecundity, nutrient availability, microbial population, and reducing HMs concentration and pathogenic microbes (Malinska et al. 2017; Mupondi et al. 2018; Paul et al. 2020). Both additives/ameliorants (biochar and phosphate rock) have also been reported as being effective in HMs passivation in biosolids and biowastes composting as discussed in the next section. Adding bamboo charcoal and earthworm mucus to domestic sludge reduced the total HMs (Cd, Pb, Ni, Cu, and Zn) concentration and the bioavailability (Huihui et al. 2022).

Thermophilic composting decreased the percentage available fraction of Cr in biogas residue while vermicomposting removed 23-31% of Cr using 0.7-1.0 g size earthworm at 60 g earthworm/kg of biogas residue (Ning et al. 2021). It was also reported during composting of lawn waste with kitchen waste and buffalo dung that vermicomposting significantly declined the concentration of HMs (Cd, Cr, As, Pb, Co, and Cu) (Karwal and Kaushik 2021). Therefore, unlike composting that has no impact (or may increase the total HMs concentration) on total HMs concentration but reduces the bioavailable content, vermicomposting can reduce total metal concentration and bioavailable concentration. A combination of woodlice and earthworms was beneficial in improving compost quality and lowering the total concentration of HMs (Pb, Cd, and Ni) with woodlice showing a greater bioconcentration factor (Ahadi et al. 2020). Generally, the effect of vermicomposting on reducing HMs concentration and availability appears to be effective, and this effect seems to be high on Cd compared to other HMs concluding from published articles.

Composting with Mineral and Organic Additives and Effect on HMs Bioavailability

Based on the effective impact of thermophilic composting on HMs passivation, additives that can prolong the thermophilic phase (or increase the peak temperature of this phase) are likely to encourage HMs passivation in compost.



Consequently, additives that promote OM degradation and humification promote the passivation of HMs and the conversion of exchangeable and reducible HMs to oxidisable and residual forms.

Clay Minerals and Related Compounds

The use of zeolite of different grain sizes (0.1 mm and 3–5 mm) in composting showed zeolite of 3-5 mm to increase the thermophilic temperature and HMs passivation (Cui et al. 2021b). The effect on Cu, Pb, and Cd was better than that on Zn and Cr in the order Cu > Pb > Cd > Zn > Cr. Results indicated that the compost significantly reduced the bioavailability factor of HMs, especially for Cu (45.13%), Pb (25.49%), and Cd (16.11%). The redundancy analysis (RDA) and structural equation models indicated that zeolite accelerated the passivation of Cd and Pb through surface adsorption by regulating the electrical conductivity, and on Cu by influencing total organic carbon through improved humification. Similarly, the use of medical stone of variable size (0.1 mm and 3-5 mm) improved available P and HMs passivation (Cu > Pb > Cd > Zn) with 3-5 mm size stone having a superior effect (Cui et al.2021a). Hence, a decrease in additive particle size may not enhance HMs passivation in composting as may be assumed. The higher grain size increased thermophilic temperature by 4 degrees C through improved aeration and heat transfer. This will improve microbial activity, which will, in turn, improve humification, and possible HM passivation through microbial activity or organo-metal complexation. It had a poor effect on Zn with a bioavailability factor of 6.1% when compared to Cu (48.05%), Pb (20.65%), and Cd (15.58%). Labile available P fraction increased by 6.45%, and this could be the factor behind Pb passivation. Black tourmaline shortened the maturity period of composting and promoted the transformation of organic substances to a stable form (Ren et al. 2020). It enhanced the binding of Zn and Cu to HA and subsequently reduced their bioavailability. A 5% application of peat in sewage sludge composting improved microbial community structure and reduced the bioavailable concentration of Zn, Cu, and Pb (Qiu et al. 2021).

Agricultural waste composting amended with attapulgite attained thermophilic phase faster with a longer duration when compared to control (Chen et al. 2022a, b, c, d). The reduction in HMs (Cd, Cr, and Zn) bioavailability was also higher in amended waste than in control with HMs passivation in the order Cd > Zn > Cr. Attapulgite promoted the conversion of the HMs to more stable forms by *Pseudomonas*. The bacterial phyla Firmicutes, Proteobacteria, Bacteroidetes, and Actinobacteria had the highest relative abundance throughout the composting. These bacteria phyla have been implicated in the propagation and maintenance of ARGs (Qui et al. 2021). HMR genes have a relationship

with ARGs through co-selection, therefore the presence of these phyla can improve HM passivation in compost. The OM and pH were the main determinant factors in attapulgite amended composting, while C:N ratio and temperature were the main factors in the control pile. Calcium-bentonite application (0–10%) in pig manure composting decreased the bioavailable fraction of Zn and Cu by 5-16% and 20-49%, respectively, when compared to control (Zhao et al. 2018). The 10% calcium-bentonite application was reported in the study, as a better rate for reducing HMs bioavailability and restricting the bioavailability of HMs after soil application. An earlier study recommended bentonite application at < 5%for HMs passivation and improvement of composting process in sewage sludge (Zhou et al. 2017). The difference in composting feedstock may be the reason behind varying recommendations of application amount. That being the case, every composting should be treated based on the specificity of its feedstock.

Natural zeolite, artificial zeolite, and expanded perlite were applied separately in sludge composting for HMs binding and removal (Ozdemir et al. 2020). Artificial zeolite and natural zeolite reduced the HMs concentration differently depending on the metal, but both were superior to expanded perlite. Artificial zeolite reduced the HMs (Fe, Mn, and Cr) by 29.9%, 35.8%, and 43.7%, while natural zeolite reduced HMs (Pb, Zn, Ni, and Cu) by 21.2%, 21.1%, 22.2%, and 24.5%. The adsorption behaviour of the adsorbents and HM selectively can be attributed to structural differences (with regard to surface area and pore size), and the mobility of the HM fractions during composting. The mobility and release of Cr, Mn, and Fe were the highest, while that of Pb, Ni, and Zn were the lowest. The natural zeolite had a smooth structure compared to the artificial zeolite and expanded perlite. Despite the rough surface of expanded perlite, it had a poor sorption effect on the HMs, and this could be due to the loss of important functional groups (through heating at high temperatures) that could bind HMs. However, the quantity of expanded perlite used in the study is half of the quantity of the different zeolites, and this could also contribute to the observed result.

Zeolite and sepiolite improved HM passivation in sewage sludge compost (Chu et al. 2023) and chicken manure composting (Wu et al. 2023). Sepiolite amendment (3%, 6%, 9%, and 12%) in pig manure composting enhanced the transformation of reducible HMs fraction to oxidisable fraction and reduced the bioavailability of Cu and Zn by 11–16% and 15–27%, respectively, when compared to control (Zheng et al. 2022). Sepiolite increased the aromaticity and percentage of HA, and the HA positively correlated strongly with oxidisable fractions of Cu and Zn. Hence, the structure of HA may play a role in its interaction with HMs. This is supported by the report that the stability constant and functional groups of HA affect its HMs binding and immobilisation



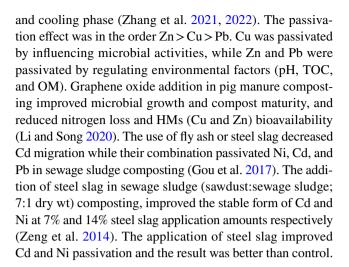
effect in the solid phase (Li et al. 2019a, b, c). Additives that improve the HA stability constant and functional group will enhance HMs complexation by HA. Montmorillonite at a 10% application reduced the bioavailability of Cu and Zn by improving residual fractions of the HMs and improved the bacterial community structure in chicken manure composting (Hao et al. 2019). Generally, clay minerals and related compounds appear effective for improving composting and reducing HMs bioavailability as shown in the literature.

Lime and Its Combination

Generally, HMs mobility increases in relation to the acidity of a system. Lime application is expected to reduce HM mobility by stabilising the pH of the composting system. A combination of zeolite (10-30%) and lime (1%) in biosolid composting improved the humification, degradation, enzymatic activities, and reduced the bioavailability of Cu and Zn (Awasthi et al. 2018). All zeolite application amounts improved the humification and reduction in HMs bioavailability, which positively correlated with higher zeolite application amount. Attapulgite-activated carbon composite and lime were added as ameliorants in swine manure composting, and the former proved to be superior in HMs immobilisation (Lin et al. 2021). High HMs content suppresses antibiotic degradation, but the immobilisation of HMs by attapulgite-activated carbon composite, through precipitation and surface adsorption alleviated this effect. Lime addition increased pile temperature with a short-term effect on HMs passivation as the effect did not increase as composting progressed. Lime application accelerated compost maturity, promoted HA generation and antibiotic degradation, and transformed exchangeable and reducible Zn into oxidisable and residual forms with a minor effect on Cu transformation (Chen et al. 2021a, b, c, d). The minor effect on Cu as observed may depend on the ionic form of Cu, either cuprous or cupric ions as the former is more soluble and is the predominant form of Cu at pH < 7. The total concentration of the HMs increased due to a reduction in the weight/ mass of the wastes through organic matter decomposition during composting. Overall, single use of lime is not effective in passivating HMs in composting. Its combination with mineral and organic additives should be employed to achieve the desired outcome.

Activated Carbon, Graphene, Fly Ash, and Steel Slag

These materials are widely applied for use in waste management and remediation of contaminated environments. Activated carbon added at different stages in chicken manure composting had varying effects on HM passivation. Addition at the thermophilic phase was best for HMs (Zn, Cu, and Pb) passivation compared to addition at the initial phase



Phosphates and Sulphates

The addition of KH₂PO₄ and FeSO₄ in sewage sludge composting reduced the mobility factor of Zn, Cu, and Pb with the least effect on Pb and the highest effect on Zn (Wang et al. 2020). The combination of both additives prevented stable Cu from transforming into mobile forms and promoted the formation of stable Pb. Calcium magnesium phosphate (CMP), monopotassium phosphate (MKP), and a mixture of MKP and ferrous sulphate (FS) passivated and stabilised HMs (Cd, Zn, Cu, and Pb) in sewage sludge composting at varying extents depending on the metal (Wang et al. 2019a, b, c). CMP had a better effect on reducing the mobility of Zn, Cu, and Cd, while MKP was good in stabilising Pb and Cd. The additives were 14–30%, 8–13%, 12%, and 20–25% better than control in reducing the mobility factor of Pb, Cu, Cd, and Zn, respectively. Cu and Zn may have been passivated during composting through the formation of CuFeS₂ and ZnCu(P₂O₇) crystals. TK correlated positively with residual Pb and Cr (Xu et al. 2022), and this could be the reason behind the inactivation of Pb by MKP additives. K₂HPO₄ was better than H₃PO₄ and H₂SO₄ in improving bacterial diversity and HMs (Mn and Zn) stabilisation with pH as a major factor than bacteria activity (Wu et al. 2021). Phosphate amendments (CMP, phosphate rock, and MKP) were used in sewage sludge composting; MKP and phosphate rock showed efficient passivation on Cd and Pb through transformation to stable crystals (Zheng et al. 2020). Phosphate rock and MKP were 27% and 25.7% better than the control in reducing the mobility factor of Pb, respectively. The use of phosphate amendment had no negative impact on seed germination as determined through germination index. Due to the mechanism of transforming HMs into stable crystalline compounds, pH is a critical factor in phosphate application.

Pig manure and cornstalk (85:15 wet wt) amended with additives (phosphogypsum 7.5% + CaO 2.5%;



superphosphate 7.5% + CaO 2.5%; zeolite 10%) at 10% application (dry wt), passivated HMs (Cd, Cu, Cr, Zn, and Pb), and reduced their bioavailability (Liu et al. 2022a, b, c). Phosphogypsum + CaO was the best amendment for HMs passivation and bioavailability reduction, and there was not much difference between the effects of other additives and control. Control was better than other additives (except phosphogypsum + CaO) in passivation and reducing the bioavailability of Cu. This is contrary to earlier reports that zeolite could passivate Cu (Ozdemir et al. 2020; Cui, Ou, et al., 2021b). Control was also better than all additives in Cr passivation. Only Phosphogypsum + CaO reduced the bioavailability and improved the passivation of Zn. The passivation rate of Cr, Cd, and Pb positively correlated with pH, HA, and HA/FA, while it negatively correlated with VFAs and N-containing substances. Phosphogypsum + CaO was 16.4%, 16.7%, and 22.1% better than control in passivation of Cu, Cd, and Pb, respectively. Animal manure composting using superphosphate and calcium carbonate, passivated HMs (Zn, Cu, Pb, and Cr) at 19.23%, 58.61%, 46.95%, and 46.20%, respectively, through reducing the exchangeable fractions of the HMs (Cui et al. 2019a, b). Calcium phosphate (5% and 10% application) in composting (swine manure, sewage sludge, mushroom residue, and sawdust) passivated Cu, Ni, and Zn. The 10% application was better than 5% with a greater passivation on Zn. Cu and Ni were passivated through complexation with HA, while Zn was passivated through the formation of stable compounds (Bao et al. 2023).

A combination of sepiolite, biochar, and CMP was better in the passivation of HMs (Ni, Zn, As, and Pb) than a single use of each in chicken manure composting (Luan et al. 2020). The additive improved organic matter humification, increased HS and HA fraction, and reduced FA fraction. Biochar has surface functional groups, porous structure, good ion exchange abilities, and high specific surface area for microbial activity that could help HMs passivation. Additives (biochar, CMP, and spent mushroom substrate) at 10% (dry wt) application were used in pig manure (with corn stalk) composting to determine their effect on HMs passivation (Kong et al. 2022). All additives improved humification, increased composting temperature, and enhanced degradation of organic matter. Cu was best passivated by biochar, Zn was best passivated by CMP at 13.85%, while others (Cd, Cr, and Pb) were best passivated by spent mushroom compost at 25.47–25.91%. The major route of HMs passivation by the additives is through promoting humification. Decrease in the availability of Cu correlated with a decrease in OM and an increase in pH and humification. Zn could form complex crystals with released phosphate, and the formation of humus (HA) with hydrophilic groups (hydrophobic organic acids) in spent mushroom substrate could form complexes with HMs.

Phosphate Rock and Boron Waste

The application of phosphate rock (PR) in animal manure composting altered and improved the bacterial community and reduced the bioavailability of HMs through passivation (Cui et al. 2021a, b, c). Proteobacteria, Bacteroidetes, and Deinococcus-Thermus were responsible for regulating transformation, controlling passivation, and regulating mobility of HMs, respectively. PR and boron waste enhanced composting humification and conversion of mobile Cu to stable Cu with a slight effect on Zn during swine manure composting (Liu et al. 2022a, b, c). FA could bind Cu and Zn as both HMs showed over 80% complexation with FA. The improved humification (HA/FA) by the additives had a greater effect on Cu redistribution. Zn has a relatively weak binding affinity with HA, which was the reason for the observed slight effect (Liu et al. 2022a, b, c), and this is supported by an earlier study, where 92-94% of Zn remained in FA despite thermophilic composting (Kulikowska and Gusiatin 2019). The addition of phosphate tailing in sewage sludge composting lowered leaching and enhanced HMs (Cu, Cr, Zn, Pb, Cd, As, and Ni) stability, and the final product was good for land reclamation (Li et al. 2018). The stable residues of Pb, As, Zn, and Cd in the compost with phosphate tailing were 15.9%, 28.18%, 14.45%, and 19.5% better than control, respectively.

In addition, boron waste and PR in swine manure-rice straw composting promoted the transformation of exchangeable and reducible Cu to oxidisable form with a slight effect on the bioavailability factor of Zn (Wang et al. 2021). The conversion of exchangeable Zn to reducible Zn can reduce Zn mobility. PR had a stronger passivation effect on Cu than boron waste at the same dose as both had a slight effect on Zn fractions. Electrical conductivity and OM were reported as important factors, and the additives promoted HM passivation by improving OM degradation. Cu had more affinity to HA than Zn, hence both additives promoted Cu passivation through HA chelation, whereas Zn by coprecipitation with phosphate. A similar study reported a better stability constant for Cu-HA complexes than Cd-HA complexes due to the difference in complexing ability with HA (Li et al. 2019a, b, c). Nonetheless, PR is more effective for Cu reduction than Zn. Extra phosphate additive (e.g. CMP) with a better passivation effect on Zn should be added with PR if Zn is the HM of interest.

Fenton-Like Processes

Fenton-like process enhanced the passivation of HMs and promoted the production of HS in the co-composting of rice straw and sediment (Chen et al. 2021a, b, c, d). The process was effective in passivating Cu and Cd but had no significant effect on Pb. Similarly, a Fenton-like system passivated HMs



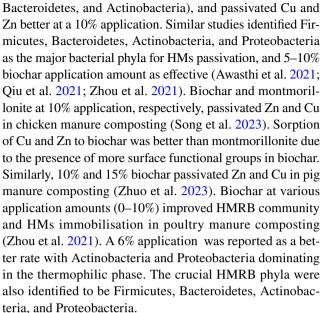
(Cu and Zn) by promoting HA formation, bacterial community, and transformation of HMs to residual form (Chen et al. 2022a, b, c, d). Furthermore, a Fenton-like reaction passivated HMs (Zn, Ni, and Mn) and influenced the removal of ARGs in fresh dairy manure composting (Niu et al. 2022). Fenton process was induced in dairy manure-sawdust composting using cuprous chloride and hydrogen peroxide. Control setup passivated Cu and Ni, while the induced compost passivated Zn, Ni, and Mn. The addition of cuprous chloride affected the effect of the Fenton process on Cu passivation. The HMs were passivated through improved humification, microbial enzyme activities, redox reactions, chelation, and complexation with HA and HS. The induced compost reduced the extractable form of Zn, Mn, and Ni better than the control by 8.46%, 7.04%, and 9.18%, respectively. It also increased the stable form of Zn and Ni better than the control by 6.12% and 5.63%, respectively. This effect is low when compared to that from other additives/ameliorants discussed above.

Others

Electric field was used to improve composting and immobilise HMs (Cao et al. 2021). Bacterial abundance, HS, HA, and bacterial activities were enhanced. The HA could bind HMs (As > Cu > Zn > Cd in order of increasing complexation) because of the promotion of HA production by electric field. Corn stalk wood vinegar at 0.65% application rate passivated Cu and Zn in Cow dung (Zhou et al. 2020a, b). A similar article also reported wood vinegar as an effective additive for improving compost quality and reducing HM toxicity in single and multi-metal contamination (Liu et al. 2018). In addition, microwave treatment of biosolids was recommended as a cost-effective method of reducing HM concentration in biosolids, as it effectively reduced the concentration of Pb and Cd (Li et al. 2019a, b, c). Table 1 shows the impact of various additives at varying application rates on HMs immobilisation, passivation, and bioavailability in compost.

Biochar as an Additive for HMs Passivation in Composting

Biochar does not reduce the total concentration of HMs in compost during composting but reduces the bioavailable concentration of the HMs (Qian et al. 2019). The breakdown of OM reduces substrate volume as labile organic matter, and it is converted to stable humus (Duan et al. 2021). Biochar addition led to fast attainment of thermophilic phase (4 days), highest peak thermophilic temperature (63 degrees C), and longer thermophilic duration (12–14 days) (Duan et al. 2021). It reduced gaseous emission (N₂O, CH₄, and NH₃), improved bacterial diversity (Firmicutes,



Biochar from different feedstocks (wheat straw, rice husks, and peanut shells) were applied to swine manure composting at various amounts to obtain the effect of feedstock and application amount on HMs passivation in composting (Chen et al. 2020a, b, c). Wheat straw-derived biochar at a 10-13% application was better than other biochar (from other feedstocks) at the same and different application amount. The difference with wheat straw biochar may be attributed to enhanced specific surface area, high porosity, and improved functional groups, which aided HM adsorption. Biochar at a 10% application passivated HMs and reduced bioavailability factor through the interaction of bacterial community and C:N ratio (Cui et al. 2020). The order in reduction of bioavailability factor was given as Cu > Pb > Cd > Zn. Biochar at 5% application in hyperthermophilic composting of dewatered sludge reduced the bioavailability of Cu, Zn, and Pb (Qin et al. 2022). Biochar was 2.4–8.7% better than controls for the amount of mobile Cu, and 3.7-19% better than controls for the proportion of residual Pb. Similarly, 10% biochar addition passivated Cr, Pb, Cu, Zn, Cd, and As better than control at 32.95%, 40.96%, 26.97%, 24.12%, 21.03%, and 15.25%, respectively (Ezugworie et al. 2022). Biochar addition in sludge composting had a significant effect on HMs (Cd, Cu, Zn, Pb, and Ni) passivation when compared to the non-significant effect observed in the control (Zhou et al. 2019). Biochar had no significant effect on the total concentration of the HMs but improved HMs passivation and reduced the bioavailable concentration. Zn and Ni were more significantly passivated by biochar addition, and the passivation of the HMs ranged from 16.39% to 43.10%. However, biochar did not show a significant effect on available HMs in soil after sludge compost application, despite showing some degree of passivation on available



Table 1 Selected literature on impact of various additives on HMs in composting

Feedstocks	Ratio	Moisture (%)	C:N	Days	Additive amount	Better additive rate and impact on HMs	Mechanism	References
Biosolids and wheat straw	5:1 w/w wet wt	55	25	56	10%, 15%, and 30% (zeolite); 1% (lime; Ca(OH) ₂) dry wt	30% Zeolite + 1% Lime better in compost humification and HMs passivation but 10% Zeolite + 1% Lime was recommended due to economic reasons	Improved humification and microbial enzy- matic activity	Awasthi et al. (2018)
Rice straw and sediment	NA	9-09	30	62	Fe ₃ O ₄ (0.5%) nanomaterials (20 nm) and CaO ₂ (1%)	Passivated Cu and Zn. Improved bacterial community and HA	Promoting HA formation, bacterial community, and HM residual frac- tion	Chen et al. (2022a, b, c, d)
Fresh dairy manure and sawdust	₹z	65	25	46	(0.2 M, 500 ml) Hydrogen peroxide and (10 g) cuprous chloride	Passivated Zn, Ni, and Mn. Poor effect on Cu, due to presence of cuprous chloride	Improved humification, microbial enzyme activities, redox reactions, chelation, and complexation with HA and HS	Niu et al. (2022)
Rice straw and sediment	5:4 w/w dry wt	09	30	50	Fe_3O_4 (1%) nanomaterials (20 mm) and oxalic acid (1%)	Significantly passivated Cu and Cd but not Pb	Improved production of HS	Chen et al. (2021a, b, c, d)
Pig manure and rice husk	2:1 w/w wet wt	65	25	30	2% Lime (dry wt)	Greater passivation effect on Zn than Cu	Promotion of HA genera- tion, and transforma- tion to oxidisable and residual forms	Chen et al. (2021a, b, c, d)
Swine manure and maize straw	1:3 v/v	09	15	52	5% Zeolite and 5% medical stone (wet wt)	3–5 mm grain size better than 0–1 mm for HMs passivation and P activation. Zeolite passivated HMs in the order Cu > Pb > Cd > Zn > Cr, while medical stone in the order Cu > Pb > Cd > Zn	Surface adsorption, improved humification, available P, and thermo- philic phase	Cui et al. (2021a, b)
Swine manure and maize straw	2:3 w/w	09	NA A	52	10% Phosphate rock	Modified microbial community, passivated HMs, and reduced bioavailability factor	Microbial regulation of transformation, mobil- ity, and passivation of HMs	Cui et al. (2021c)
Pig manure and straw	3:2 v/v	60 – 65	25	30	2.5%, 5%, 7.5% coal ash; 2.5%, 5%, 7.5% phosphate rock; and 7.5% sepiolite	2.5% coal ash, 5% phosphate rock, and 7.5% sepiolite passivated Cubetter than other percentage combinations	Transformation of Cu to residual forms	Lu et al. (2015)



Page 16 of 28

Table 1 (continued)								
Feedstocks	Ratio	Moisture (%)	C:N	Days	Days Additive amount	Better additive rate and impact on HMs	Mechanism	References
Pig manure and sawdust	5:3 w/w	92	20	09	3%, 6%, 9%, 12% sepiolite	Reduced Cu and Zn bio-availability	Improved HA structure and stability	Zheng et al. (2022)
Sediment, straw, bran, and 20:22:4:2 w/w dry wt NA vegetable	20:22:4:2 w/w dry wt	N A	33	62	2% attapulgite (dry wt)	Reduced bioavailable concentration of Cd, Zn, and Cr with a greater effect on Cd and Zn	Improved thermophilic phase and thermophilic duration. Increase in HM residual fractions through microbial activities	Chen et al. (2022a, b, c, d)
Chicken manure and rice husk	NA	09	25	09	10% Montmorillonite (dry wt)	Reduced the bioavailability of Cu (81.2%) and Zn (15.6%)	Improving microbial community structure and HM residual fractions	Hao et al. (2019)
Pig manure and corn stalk NA	NA	NA	20	28	0.1%, 0.25%, 0.5% graphene oxide (dry wt)	0.5% better for Cu and Zn bioavailability reduction	Improved microbial activity	Li and Song (2020)
Wet swine manure and mushroom residue	1:1 w/w	NA	NA	42	7% Attapulgite-activated carbon (5:1 ratio) composite and 1% lime	Attapulgite-activated carbon composite caused 4-64% HMs immobilisation and was superior to lime	Precipitation and surface adsorption	Lin et al. (2021)
Fresh swine manure and pulverised rice straw	1:2 v/v	NA	NA	49	5% Phosphate rock and 5% boron waste	Boron waste showed stronger passivation on Cu but neither additive altered Zn fractions	Improving OM degrada- tion, and transformation to stable fractions	Liu et al. (2022a, b, c)
Sewage sludge and hazel- nut husk	Υ _Α	60 - 65	30	09	10g Natural zeolite, 10g artificial zeolite, 5g expanded perlite	Natural zeolite reduced Fe (29.9%), Mn (35.8%), Cr (43.7%), artificial zeolite reduced Pb (21.2%), Zn (22.1%), Ni (22.2%), Cu (24.5%). Expanded perlite had poor effect	Surface adsorption	Ozdemir et al. (2020)
Poultry manure and sawdust	2:1 w/w dry wt	65	30	42	5% and 10% Black Tourmaline (TM)	TM improved the complexation of Zn and Cu with HA and reduced FA binding. 10% TM was better than 5%	Improved humification and enhanced binding of HMs to HA	Ren et al. (2020)



Table 1 (continued)

Zhang et al. (2021, 2022) Wang et al. (2019a, b, c) Zheng et al. (2020) Wang et al. (2021) Wang et al. (2020) Qiu et al. (2021) Wu et al. (2021) References Improved bacterial activ-Transformation to stable HMs to stable fractions Formation of stable HM phase and humification Improved humification and transformation of Improved thermophilic Improved thermophilic philic phase duration, temperature, thermo-Improved stability of HMs and prevented transformation to and humification ity by K₂HPO₄ mobile forms Mechanism crystals crystals Zn, Cd, and Cu followed Pb stabilisation and pasapplication at initial and factor of Zn, Cu and Pb on reducing mobility of by mixture of MKP and FS. MKP was best for philic phase better than CMP had superior effect cooling phase for HMs additives can passivate Cu and Zn. 7.5% phosthan other application and bacterial diversity Cu, Pb) concentration Cd and Pb passivation Better additive rate and Reduction in HMs (Zn, and removal of patho-R and MKP better for availability of Cu and phate rock was better for HMs stabilisation Application at thermorate of both additives mobility of Zn. Both reduced the mobility than other chemicals 2.5-7.5% application Combination of both K₂HPO₄ was better reduced the biogenic bacteria mpact on HMs improvement passivation sivated Cd amounts 7% activated carbon (w/w) 1% Phosphate salts (MKP, .25% KH₂PO₄ and 1.25% H,SO₄ at 0.25 mol mass mixture of 0.5% FS and superphosphate) and a sium phosphate, 2.5% 2.5% monopotassium 2.5%, 5%, and 7.5% of hydrogen phosphate, phosphate rock, and Phosphate rock and H₃PO₄, K₂HPO₄, and 2.5% calcium magne-CMP, dipotassium FeSO₄ (wet wt) per kg (dry wt) Additive amount boron waste 0.5% MKP phosphate 5% Peat Days 45 18 49 9 42 21 20-25 $C: \Sigma$ NA ΝĀ Ϋ́ Ϋ́ 20 Moisture (%) 55-60 NA ΝA 55 9 9 4:3:1 w/w wet wt 4:3:1 w/w wet wt Pig manure and corn stalk 5:1 w/w wet wt 3:2 v/v Ratio Dewatered sewage sludge, 6:3:1 Fresh chicken manure and 1:20 ΝA Dewatered sewage sludge, Maize straw and sewage Swine manure and rice spent mushroom submushroom substrate, Sewage sludge, spent returning compost, strate, perlite and perlite Feedstocks sawdust sawdust straw



HMs in soil. This calls for more understanding of the longterm effect of biochar-passivated HMs in soil application to prevent soil contamination and plant accumulation.

Modified Biochar and Biochar in Combination with Other Additives

Modified biochar and a combination of biochar with other composting additives/ameliorants appear to be more effective in HM passivation than a plain/single use of biochar. A combination of biochar and HA in pig manure composting led to 94.98%, 68.78%, and 65.55% passivation in Cu, Cd, and Pb, respectively (Zhou et al. 2018). Application of the final compost in the soil further reduced exchangeable fractions of the HMs in the soil and reduced the accumulation of the HMs in plants. Biochar and H₃PO₄-modified biochar reduced the extractable Zn and Cu concentration in swine manure composting (Chen et al. 2022a, b, c, d). H₃PO₄-modified biochar was better than biochar and the effect on Zn was higher than that on Cu. The immobilisation effect of H₃PO₄-modified biochar was through the formation of a metal-phosphate precipitate, and this explains its effect on Zn through the formation of Zn-phosphate complexes. H₃PO₄ caused a surface modification in biochar leading to a product with higher surface area and enhanced sorption efficiency.

Montmorillonite and biochar increased the diversity of actor Zn/Cu bacteria hence promoting HMs passivation (Song et al. 2021). The organic fractions (HA, humus, FA, and DOM) played an indispensable role in deactivating the HMs by interacting with the actor bacteria. Graphene-modified biochar was better than non-modified biochar in improving the composting process, reducing N loss, improving compost quality, and in passivation of Zn and Cu (Song et al. 2020). There was a 25% increase in HM passivation using graphene-modified biochar when compared to non-modified biochar, and both were better than the control.

A mixture of biochar and microbial inoculum immobilised Cu and Zn through improved HA and FA generation (Li et al. 2019a, b, c). The immobilisation of the metals positively correlated with humification during composting of pig manure. Integration of biochar (12%) with bacterium culture had a better effect on immobilising HMs (Cu and Zn) through improved adsorption and improved bacterial community structure (Awasthi et al. 2020). The combination of 12% biochar and microbial inoculum was better than a single use of 12% biochar and a single use of inoculum. Table 2 summarises the effect of biochar, modified biochar, and a combination of biochar and other additives in HMs passivation.

Conclusion and prospects

Composting favours the transformation of exchangeable and reducible HMs to oxidisable and residual forms thereby reducing their mobility, leachability, and bioavailability. Humification of composting feedstocks through biomass degradation plays a major role in HMs passivation during composting. Microbes and macro-organisms improve humification thus enhancing HMs passivation through binding and complexation with HS. The use of additives/ameliorants in composting enhances the reduction of HMs bioavailability through improved humification, microbial activities, physicochemical properties, and other processes. Additives that improve humification, microbial community structure, and thermophilic phase are more effective for HMs immobilisation and passivation in composting. Microbes play a principal role in composting and HM passivation and their activity is the key determinant of composting success.

Though improved humification and formation of organo-metal complex contribute to the passivation of all HMs in composting, this impact is more effective on Cu, with some level of improved effect on Zn, Cd, and Pb. Vermicomposting had more effect on Cd, and hyperthermophilic composting was more effective on Pb. Biochar and clay minerals can passivate all HMs, while phosphate is more effective on Zn, Cu, Pb, and Cd. CMP showed more efficiency on Zn, Cu, and Cd, while PR and MKP showed more efficiency on Pb and Cd. Zn, Cu, and Pb can form complex compounds with phosphate, hence enhancing their passivation. Microbial inoculation and vermicomposting are better options for Cr, Ni, Fe, and Mn, due to various microbial mechanisms of which biosorption and bioreduction have greater effect.

However, considering the varied nature of additives, and their mechanisms of action, it is difficult to establish the optimum amount of additive required to enhance the reduction of bioavailability of HMs during composting. It is also tough to decide the best additive option for a given HM or HMs in composting. Researchers always arrive at different conclusions on which HM was passivated. This makes the choice of additive challenging, but adding ligneous bulking agents is unarguably beneficial. Therefore, we propose a combined additive method based on HMs of interest. Biochar and clay minerals are effective on all HMs, so they can be utilised to passivate any HM, with the addition of other additives. Vermicomposting of final compost is beneficial and should be considered for passivation of any HM, but this should be highly considered if Cd is involved. Vermicomposting can also reduce total HM content due to the bioaccumulation efficiency of earthworms, especially Eisenia fetida. Phosphates should be used with biochar/clay minerals to passivate Cu, Zn,



Table 2 Selected literature on effect of biochar addition on HMs in composting and co-composted biochar

Hatio Biochar feedstock Pyrolysis temp. (°C) Moisture, C.N, & duration Wheat straw, Rice 500 (3h) 65%, 25:1, and 35 husk, and peanut shells and 5:1 w/w Wheat straw 500 (4h) 66%, NA, and 42 days and 1:3 v/v NA NA NA NA 65%, NA, and 52 days anure NA Pruned apple 500–550 (7-8h) 65%, 25:1, and 49 raw branches days				•				
NA Wheat straw, Rice 500 (3h) 65%, 25:1, and 35 husk, and peanut shells 5:1 w/w Wheat straw 500 (4h) 60%, NA, and 42 days 1:3 v/v NA NA NA 65%, NA, and 52 days NA Pruned apple 500–550 (7-8h) 65%, 25:1, and 49 branches days		Biochar feedstock	Pyrolysis temp. (°C)	Moisture, C:N, & duration	Biochar amount	Effect on HMs	HMs passivation mechanism(s)	References
5:1 w/w Wheat straw 500 (4h) 60%, NA, and 42 days 1:3 v/v NA NA NA 65%, NA, and 52 days NA Pruned apple 500–550 (7-8h) 65%, 25:1, and 49 branches days		Wheat straw, Rice husk, and peanut shells	500 (3h)	65%, 25:1, and 35 days	2%, 5%, 7%, 10%, 13% w/w	10–13% wheat straw better than other rates and other biochar feedstock. Reduced Cu and Zn accumulation in crops when the co-composted biochar was	Improved microbial growth leading to transformation of exchangeable HM fractions to residual fractions. Biochar HMs interactions and sorption	Chen et al. (2020a, b, c)
1:3 v/v NA NA 65%, NA, and 52 days NA Pruned apple 500–550 (7-8h) 65%, 25:1, and 49 branches days		Wheat straw	500 (4h)	60%, NA, and 42 days	10% w/w of biochar and 20% H ₃ PO ₄ -modified biochar respec- tively	H ₃ PO ₄ -modified biochar was better than non-modified biochar. Reduction effect of modified and non-modified biochar on Zn (37%; 27%), Cu (15%; 12%) respectively	Formation of HM-phosphate precipitate. Higher sorption due to increased surface area	Chen et al. (2022a, b, c, d)
NA Pruned apple 500–550 (7-8h) 65%, 25:1, and 49 branches days		Υ Z	₹ Z	65%, NA, and 52 days	5%, 10% w/w (dry wt)	10% better than 5% with a greater effect on Cu and Pb compared to Cd and Zn	Improved micro- bial activity, humification, and transformation to residual fractions	Cui et al. (2020)
	sheep manure NA wheat straw	Pruned apple branches	500–550 (7-8h)	65%, 25:1, and 49 days	2.5%, 5%, 7.5%, 10%, 12.5%	Passivated Zn and Cu at all amounts but 10% application rat was better than others	Improved ther- mophilic phase, microbial com- munity, and high pH	Duan et al. (2021)
Corn stalk 300–450 60%, 25:1, and 60 days	chicken NA ure and rice	Corn stalk	300-450	60%, 25:1, and 60 days	10% w/w (dry wt)	Passivated Zn (56.4%) and Cu (76.4%)	Transformation to oxidisable and residual fractions through improved microbial activity	Hao et al. (2019)



Table 2 (continued)								
Compost Feed- stocks	Ratio	Biochar feedstock	Pyrolysis temp. (°C)	Moisture, C:N, & duration	Biochar amount	Effect on HMs	HMs passivation mechanism(s)	References
Pig manure and corn straw	9:1 w/w	Sawdust, corn straw, and peanut shell	009	65–70%, 25:1– 30:1, and 30 days	Biochar @ 6%, 12%, and 24% dry wt. Micro- bial inoculum @ 0.5%, 1.0%, 1.5% dry wt	70.36% Cu immobilisation by 12% peanut shell biochar and 0.5% microbial agent. 40.76% Zn immobilisation by 24% sawdust biochar and 1.5% microbial agent	Improved humifi- cation and pH	Li et al. (2019a, b, c)
Fresh sewage sludge and straw	6:5	Straw	350–550	60%, 25:1, and 31 days	1%, 3%, 5%, 7% biochar and 0.4% microbial agent	7 5.	Improved pH, CEC, and binding to biochar func- tional groups	Liu et al. (2017)
Municipal solid waste	N A	Pigeon pea stems	300 (2h)	V.	2%, 5%, and 10%	10% and 5% Co- composted bio- char effectively reduced uptake of HMs by spinach	Complexation with stable OM, and sorption by biochar	Mounissamy et al. (2021)
Pig manure	NA A	Wood and bamboo	₹ Z	e	5% wood biochar and bamboo bio- char, graphene- modified wood biochar, and gra- phene-modified bamboo biochar, respectively	Graphene-modified biochar (for both wood and bamboo) performed better than non-modified biochar passivating HMs. Use of 5% graphene-modified wood biochar had better outcome on HM passivation	Improved humifica- tion and increase in pH, and com- plexation with HS. Promotion of propagation of HMR bacteria leading to stable transformation of HMs by bacteria	Song et al. (2020)
Municipal solid waste	NA	Khat straw	350 (4h)	70%, NA, NA	5%, 15%, and 25% w/w	5–15% biochar addition reduced HM content in final compost	Sorption by bio- char	Tessfaw et al. (2020)
Poultry manure and wheat straw	5:1	Wheat straw	550-600 (24h)		2%, 4%, 6%, 10% w/w	6% improved immobilisation of HMs	Promoting the abundance and propagation of HMRB	Zhou et al. (2021)



 Table 2 (continued)

(
Compost Feed- stocks	Ratio	Biochar feedstock	Pyrolysis temp. (°C) Moisture, C:N, & duration	Moisture, C:N, & duration	Biochar amount	Effect on HMs	HMs passivation mechanism(s)	References
Water hyacinth, cow dung, and sawdust	6:3:1 w/w (wet wt)	Prosopis Juliflora	400–500	NA, NA, and 20 days	2.5%, 5%, 10% w/w wet wt	2.5% better for composting water hyacinth. Biochar reduced Cr and Cu content	Prolonged thermo- philic tem- perature, together with direct and indirect biochar interaction	Jain et al. (2019)
Poultry litter, corn stalk, and vegeta- ble waste	57.58%, 38.41%, and 4.01%	Coconut husk	400–500	NA, 25:1–30:1, NA	5% and 10%	10% was better for HMs reduction, and OM degradation	Transformation to stable forms	Ezugworie et al. (2022)
Fresh chicken manure and corn straw	e Z	Rice straw	500 (1h)	NA, 25:1, and 30 days	10%, 20%, 30%, 40% w/w (dry wt)	10% was better and reduced the bioavailability of Zn, Cr, Ni, As, and Cd	Interaction with biochar associated organic functional groups. Interaction with pH and DOC	Li et al. (2021a, b)
Maize straw and sewage sludge	3:2 v/v	Maize straw	400 (8h)	60%, NA, and 40 days	5%	Reduction in HMs (Zn, Cu, and Pb) concentration	Improving microbial community	Qiu et al. (2021)
Sewage sludge and corn cob	5:3 v/v	NA	NA	NA, NA, and 28 days	8.2% and 15.15%	Biochar addition positively affected Zn, Cu, Pb, Ni, and Cr passivation	Binding to HS and formation of HM crystals	Liu et al. (2021)
Sediment, rice straw, bran, and vegetable	18:25:4:5 (w/w wet wt)	Rice straw	500 (2h)	65%, 32:1, and 50 days	2%	Reduced bioavailability of Cd, Zn, Cu, and Cr at 2.96%, 0.90%, 0.51%, and 0.1% better than control	Increased pH and negative charge. Sorption by biochar and binding to functional groups	Chen et al. (2017)
Pig manure and corn stalk	NA	Maize straw	600 (2h)	NA, NA, and 49 days	10%	Improved humification and organic matter degradation. Best effect on Cu passivation when compared to Zn, Pb, Cd, and Cr	Transformation to residual forms, and possible complexation with released phosphate to form insoluble crystals	Kong et al. (2022)



lable z (continued)									
Compost Feed- stocks	Ratio	Biochar feedstock	Biochar feedstock Pyrolysis temp. (°C) Moisture, C:N, & Biochar amount duration	Moisture, C:N, & duration	Biochar amount	Effect on HMs	HMs passivation mechanism(s)	References	
Dewatered sewage 3:2 w/w dry wt sludge and corn straw	3:2 w/w dry wt	Wheat straw	550	21 days	2%	Biochar improved the reduction of HMs availability when compared to control	Biochar improved Improved humifi- Qin et al. (2022) the reduction of cation through HMs availability hyperthermo- when compared philic condition. to control Transformation to residual fractions, electro- static interaction, sorption to biochar, and HM precipitation	Qin et al. (2022)	<u>-</u>

Pb, or Cd. Microbial inoculation with biochar should be considered under Cr. Ni. Fe, or Mn. HS especially HA is effective against Cu, and its combination with biochar is likely to yield a high passivation efficiency against Cu. Caution should be applied while using biochar as biochar produced from an HM-contaminated feedstock could pose more HM-related challenges, and a high biochar amount may be detrimental to microbes and soil.

HMs are not biodegraded during composting despite the positive impact of various additives. Rather, they are transformed into less toxic and less available forms. The challenge remains in monitoring and understanding the sustainability of these different passivation effects, with regard to soil application to prevent possible contamination and plant accumulation. Achiba et al. (2009) monitored compost application in soil for 5 years and reported that the HMs existed mainly in their passivated form with a low mobility factor. The concern is on how long this passivation will last. Are the HMs irreversibly passivated or will they become mobile and available under long-term application? What environmental and soil conditions can trigger remobilisation of passivated HMs? How can HM passivation be improved or possible availability in soil be prevented? What happens to the HMs accumulated in earthworm tissues at the end of their life cycle if not passivated or transformed?

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Declarations

Conflict of interest The authors declare no conflict of interest.

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