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Biochar and heavy metals

Luke Beesley, Beatriz Cerqueira Cancelo, Michael Hardman, Manhattan Lebrun, Kerry Mitchell, and Lukas Trakal

Introduction: Heavy metals in the environment

Definitions

Heavy metals in soils are derived from both geogenic and anthropogenic sources. In the case of the latter, this may be due to point or diffuse sources as diverse as mining, smelting, industrial processing, waste disposal, fertilizer, and herbicide and pesticide usage (Ross, 1994). In excessive concentration, those heavy metals regarded as the most toxic and environmentally deleterious are cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn), although several of these, especially those that are transition metals, are nonetheless essential for plant metabolism (e.g., Cu, Ni, Zn). By definition, heavy metals are a group of elements with specific gravities of >5 g cm^{-3} (Ross, 1994) which are both industrially and biologically relevant (Alloway, 1995). Although not heavy metals by chemical definition, the metalloids arsenic (As) and antimony (Sb) are given the status of "risk elements" or "potentially toxic elements" due to their impacts on humans and toxicity to plants after excessive exposure (Moreno-Jiménez et al, 2012). In that case, those heavy metal(loid)s that cause a toxic response to biota or humans resulting in an unacceptable level of environmental risk (Adriano, 2001; Abrahams, 2002; Vangronsveld et al, 2009) may be classed as pollutants. At the ecosystem level, the chemical behavior of heavy metal(loid)s in soils resulting in their mobility and toxicity are complex and, since this book is concerned with "environmental management" we will focus on interactions between biochar and heavy metal(loid)s through an environment lens. This chapter covers the main or "master" mechanisms by which biochars impact metal(loid)s in soils and discusses these via applied examples. Biochar's impacts on metal(loid)s in water is covered elsewhere in this book (Chapter 27).

Exposure and risk

Heavy metal(loid)s in soils and sediments are partitioned into a number of binding phases either (i) incorporated in the solid phase;

DOI: 10.4324/9781003297673-21

(ii) bound to the surface of the solid phase; (iii) bound to ligands in solution; or (iv) as free ions in solution. Only the free ions in solution (i.e., phase (iv)) can be taken up by organisms and, therefore, only the free ions are bioavailable (Di Toro et al, 2001; Thakali et al, 2006). In soils, there is often disequilibrium between these four phases due to contrasting geochemical conditions, though the tendency is strongly to equilibrate in the most rapid time. If the concentration of metal ions dissolved in solution decreases (for example, due to plant uptake), then equilibration will again occur by which more metals desorb to increase the amount of metal ions in solution.

To cause a toxic effect, heavy metals must dissolve into a solution, be taken up by an organism, and be transported to cells where a toxic effect can occur. This complex interaction between organisms and contaminants can be described by a simple model known as the source-pathway-receptor model (Hodson, 2010). The source of the pollution is a heavy metal (e.g., Pb), the receptor is a biological organism (e.g., an earthworm), and the pathway is the process that leads to the contaminant being taken up by the organism (e.g., desorption of Pb from the soil surface into the soil solution and diffusion across the gut wall of the earthworm). Therefore, remediation of heavy metal contaminated sites can be performed by (i) removing all or part of the source; (ii) eliminating the pathway; or (iii) modifying the exposure of the receptor (Nathanail and Bardos, 2004). Thus, remediation is achieved in heavy metal-polluted environments by reducing the bioavailability of the metals to the receptor organisms. Since heavy metals cannot be degraded or broken down (i.e., the source cannot be depleted in situ), and receptors often cannot be fully or even partially isolated in complex media, such as soils; the only viable option to break the source-pathway-receptor linkage is to disrupt the pathway between the contaminant and the receptor. Manipulation of bioavailability increasingly forms the basis of risk assessment and classification of polluted areas, rather than absolute concentrations in soils (Bolan et al, 2008; Durães et al, 2018). Importantly, in the legislative context of most nations, it is this potential to cause harm to humans or ecosystems (the effect) that defines polluted sites and not the presence (concentration) of the contaminant per se. Therefore, if biochars are to be deployed to heavy metal(loid) contaminated systems then it is their ability to break the pathway from source to receptor that becomes a focal point of their deployment (Park et al, 2011) (Figure 21.1).

Fig 21.1

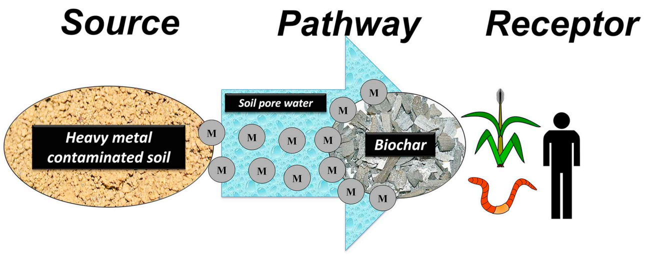

Figure 21.1 *Schematic representation of biochar disrupting the pathway of heavy metal(loid)s (M) from their source to receptor organisms*

Biochar as a remedial amendment

Biochars, in common with other organic amendments, can reduce heavy metal(loid) mobility and bioavailability by various physicochemical means (Bolan and Duraisamy, 2003). The application of organic amendments to soils, from a remedial point of view, has typically been justified by their relatively low cost, compared to "hard" engineering solutions (such as removal and disposal of soils elsewhere) as well as their prevalence as a waste, ordinarily requiring other forms of disposal (burial in landfill, incineration, etc.). The pyrolysis of organic materials to produce biochar increases the surface area and effective cation exchange capacity (CEC) compared to the unpyrolyzed source, and has a lower mineralization rate than unpyrolyzed materials (Chapter 11), theoretically requiring less frequent additions to maintain efficacy than other, more easily mineralizable organic materials, such as composts, manures, etc. Therefore, the justification for the addition of biochar to metal(loid) contaminated soil is that it can work as a sorbent for metals in solution by establishing a new equilibrium between the concentrations of metals sorbed to surfaces and that in solution. Before this chapter embarks on the detail of the mechanistic, advantageous, and disadvantageous functions of biochar, an important premise should be noted: the same features of biochar that render it suitable for remediation of heavy metal contaminated substrates may at once deem it unsuitable for application, specifically where the desired effect is to increase the bioavailability of metals. The obvious example is Zn, an essential plant nutrient and important element to fortify food and feed but, in excess, a toxin. Rather than considering absolute increases or decreases in heavy metal concentrations in substrates receiving biochars, the emphasis should be placed on bioavailability, mobility, and specific requirements related to land use.

Heavy metal-biochar interactions at the soil-water interface

Direct mechanisms

Direct mechanisms of heavy metal immobilization by biochar include, but are not limited to, fundamental chemical "at-soil surface" processes, such as adsorption and complexation. It is widely acknowledged and discussed that biochars may both mobilize and immobilize heavy metals and As by direct means such as ion exchange, chemical and physical adsorption, precipitation, etc. (Abdelhadi et al, 2017; Soria et al, 2020). These mechanisms are discussed in the following section.

Chemical sorption

During exposure to the atmosphere, such as environmental weathering of freshly produced biochars applied to soils, the oxygenation of biochars' myriad surfaces occurs (Cheng et al, 2006) forming oxygen (O) containing functional groups (e.g., carboxyl, hydroxyl, phenol, and carbonyl groups; Uchimiya et al, 2010, 2011; He et al, 2019). These functional groups induce a negative charge and a high CEC (Sorrenti et al, 2016). CEC first increases, and then decreases, with increasing pyrolysis temperatures (Harvey et al, 2011; Mukherjee et al, 2011;

Wu et al, 2016; Tomczyk et al, 2020); a peak CEC of up to 450 $\mathrm{mmol_c\,kg^{-1}}$ has been shown to occur between 250 and 350°C, depending on the source material. The lower oxygen to carbon (O/C) ratio and reduced abundance of oxygenated (acid) functional groups lowers CEC after higher temperature pyrolysis (Uchimiya et al, 2011; Harvey et al, 2011; Shen et al, 2012). The capacity for metal immobilization demonstrated by lower temperature (<500°C), and faster pyrolysis biochars (Beesley et al, 2010; Beesley and Marmiroli 2011) is therefore, in part, a result of the high CEC of these biochars; biochars with a similar CEC to the soil they are applied to will not immobilize heavy metals as effectively as biochars with greater CEC than the receiving soil (Gomez-Eyles et al, 2011, 2013). Highly weathered acidic tropical soils, low in organic C, whose mineralogy is dominated by kaolinite and iron (Fe)- or aluminum (Al)-oxyhydroxides, yield a low CEC (Schaefer et al, 2008). These soils are more readily phytotoxic than soils from temperate regions due to their inherent inability to retain heavy metals (Melo et al, 2011). In such soils, it is more likely that adding biochars will increase CEC and be more effective in immobilizing heavy metals.

Surface sorption of metals corresponds directly with the release of H^+ ions from biochars, but also of the release of Na, Ca, S, K, and Mg into the solution, which indicates retention of metals on protonated (acidic) functional groups but also metal exchange with other cations (Uchimiya et al, 2010, 2011; Park et al, 2019). Phosphorus- and sulfur (S)-containing ligands influence the sorption of metal ions such as Pb that have a stronger affinity for phosphates and sulfates (Cao et al, 2009). Biochar surface oxygenated functional groups may impact the oxidation of redox-sensitive metals whilst biochar application to soils also changes soil porosity and modifies soil physical structure, which may influence microscale redox condition. In these cases, redox-sensitive elements will change their speciation and geochemistry; for instance, As(III) is found in anoxic environments (<100 mV) and is more mobile in soils and toxic than As(V); Cr can be oxidized in aerobic environments (>300–400 mV) and Cr(VI) is more toxic than Cr(III), whilst Cu (I) can also be found under anoxic conditions.

Physical sorption

Aside from a pure ion exchange between biochar surfaces and metals, a non-stoichiometric release of protons and other cations from the surface of biochars can occur; more metals are adsorbed than protons or cations are released and sorption can occur at pH below the point of zero net charge (Sánchez-Polo and Rivera-Utrilla, 2002). The immobilization of metals by biochar cannot, in these instances, be purely attributed to ion exchange alone. Metal sorption to biochars is an endothermic physical process (Liu and Zhang, 2009; Harvey et al, 2011) and an electrostatic interaction between the positively charged metal cations and π-electrons associated with either C=O ligands or C=C of a shared electron 'cloud' on aromatic structures of biochars occurs (Cao et al, 2009; Uchimiya et al, 2010; Harvey et al, 2011).

An increase in the pyrolysis temperature of biochars increases their aromaticity whilst the abundance of oxygenated functional groups decreases (Jung et al, 2016). Thus, increasing pyrolysis temperature increases the proportion of cations sorbed due to 'weak' electrostatic bonding (i.e., cation-π interactions) and decreases the proportion due to stronger chemisorption (i.e., by cation exchange). Therefore, lower temperature pyrolysis should result in effective short-term metal immobilization due to the formation of inner and outer sphere complexes with oxygenated (acid) functional groups, but with time these may diminish in the soil environment.

Thereafter there may be a release of metals back into solution. Higher pyrolysis temperatures result in a negative surface charge that should remain stable for longer, but metals will be weakly (physically) adsorbed to biochar surfaces and immobilization may be more easily reversed (summary in Table 21.1).

Table 21.1

Precipitation

Biochar source materials are unlikely to be 100% organic in nature and contain minerals that remain entrained in the biochar matrix after pyrolysis, resulting in a non-organic (or ash) fraction in biochar. Source material mineral contents can range from <1% for woody biomass, up to ~25% for manure or crop residues. Following high-temperature pyrolysis, the ash content of biochars can be up to 50% for manure-derived or 85% for bonemeal-derived biochars. Thus, mineral salts of Na, K, Ca, Mg, P, S, Si, and C are found in abundance in the ash fraction, usually in an oxidized form, their concentrations of which increase with pyrolysis temperature. Uchimiya et al (2010) found Pb phosphate precipitates effective in immobilizing Pb in a broiler litter-derived biochar whilst precipitation of Pb with phosphates contributed to as much as 87% of total Pb sorption to a dairy manure-derived biochar (Cao et al, 2009). Lead-phosphate minerals contributing to sorption in biochars include hydrocerussite and hydroxylpyromorphite (Cao et al, 2011), Pb phosphate, and Pb hydroxyapatite (Chen et al, 2006). Lead-phosphate minerals have a very low solubility so their formation could result in the increased capability of biochars to adsorb higher concentrations of Pb, compared to other divalent cations (Uchimiya et al, 2010; Namgay et al, 2010; Trakal et al, 2011). Precipitation may also occur with other metals such as Cu, Cd, or Zn which precipitate as insoluble phosphate and carbonate salts, mainly at high pH (Lindsay, 2001).

Indirect mechanisms

Indirect mechanisms can also be defined as the effects that biochars have on soil characteristics (physical, biological, and chemical) that then impact heavy metal retention or release. The addition of biochar to soils can, amongst myriad other effects, increase soil pH, microbial biomass, organic C, and water holding capacity which may in turn impact heavy metal retention and release. This section is mainly concerned with, and summarizes the results of, studies examining pH changes induced by biochar additions to soils. Other impacts of biochar addition are briefly covered.

pH changes

It is widely reported that the addition of alkaline biochars to soils resulted in pH increases (Ippolito et al, 2017; Lebrun et al, 2020); metal solubility changes according to pH, generally being lower at higher pH. For metalloids, the geochemistry is somewhat opposing, with higher pH conditions reducing retention (Adriano, 2001). Arsenic solubility and availability increase when pH in soils rises, in most cases, since As binds to positively charged surfaces such as Fe and Mn oxides in soils and anion exchange capacity (AEC) is inversely related to pH (Moreno-Jiménez et al, 2012). Cationic metals (e.g., Cu, Zn, Pb), which are bound to the negatively charged surfaces of soils such as clay minerals and organic matter, increase in solubility as pH decreases because CEC is positively related to pH. When the soil pH increases, metals are increasingly bound to negatively charged surfaces. Contrary to cationic metals, As is released from positively charged soil surfaces when the soil pH is increased; an increase of soil pH has thus been reported to increase As mobility and uptake by organisms (Fitz and Wenzel, 2002).

Studies have reported that soil pore water pH increases after biochar application

Table 21.1 *Selected examples of the influence of pyrolysis temperature on heavy metal sorption capacity, assessed by batch sorption experiments*

Experiment	*Biochar preparation*	*Findings*	*Reference*
Batch aqueous sorption of Pb, solution added at 0.02 g biochar for 20 mL solution	Biochars produced by pyrolysis of sawdust of white spruce, canola straw, wheat straw, and manure pellet at 300°C, 500°C and 700°C	Maximum Pb(II) adsorption increased with increasing pyrolysis temperature. Sorption occurred through multilayer adsorption on the heterogeneous surface, with a finite number of sites.	(Kwak et al, 2019)
Batch aqueous sorption of Cu, solution (20 mL) added to 10 mg biochar	Biochar produced from the pyrolysis of Jerusalem artichoke stalks at 300°C, 500°C and 700°C	Highest maximum adsorption potential (Qm) measured for the low-temperature biochar (300°C, 17 mg g^{-1}). For low-temperature biochar (300°C), sorption took place on a homogeneous surface, while for high-temperature biochar (500°C, 700°C), sorption occurred on a heterogeneous surface. Sorption mainly occurred through the reduction of Cu(II) to Cu(I) (for biochars produced at 300°C and 700°C), surface complexation (importance declines with the increase in pyrolysis temperature), Cu cation-π bonding and precipitation with PO_4^{3-} (for high-temperature biochars).	(Wei et al, 2019)
Batch aqueous sorption of Cd, solution (25 mL) added to 0.05 g biochar	Biochars produced from the pyrolysis of pine cones, pine needles, and pine bark at 300°C to 600°C	Cd sorption increased with the increase in pyrolysis temperature. Sorption mechanisms were identified to be the release of phosphate, the removal of cations, and interaction with functional groups (C=C and COO).	(Park et al, 2019)
Batch sorption of Pb, solution (60 mL) added to 0.03 g biochar	Biochars from cotton straw pyrolyzed at five different temperatures, from 300°C to 700°C	Highest removal efficiency with the biochar produced at 600°C (51 mg g^{-1}). Adsorption mechanism was identified to be ion exchange with Na^+, K^+, $Ca^{2+,}$ and Mg^{2+}, cation-π interactions, and precipitation on the biochar surface, as hydroxypyromorphite and hydrocerussite. Difference of mechanism dominance with pyrolysis temperature: complexation at low temperature, precipitation at high temperature.	(Wang et al, 2021)

Table 21.1 *continued*

Experiment	*Biochar preparation*	*Findings*	*Reference*
Batch sorption of Fe, Ni, Cu, Cr and Pb	Biochars produced from the pyrolysis of bamboo, sugarcane, or neem at 450°C and 550°C	Higher removal efficiency with the high-temperature biochars. Mechanism of sorption was identified to be chemisorption, with exchange of valence electron.	(Singh et al, 2021)
Batch sorption of Pb, solution (20 mL) added to 40 mg biochar	Biochars produced from cotton stalks pyrolyzed between 250°C and 650°C	Pb removal efficiency increased with increasing pyrolysis temperature. Chemisorption identified as the dominant adsorption mechanism: formation of lead precipitates on the biochar surface (principally cerussite), cation exchange with K and Ca, complexation with oxygen functional groups, and cation π interactions with other functional groups (C=C, -CH), and electrostatic interaction.	(Gao et al, 2021)
Batch sorption of Cd, Pb, and Zn, solution (100 mL) added to 10 g biochar	Biochars produced from the pyrolysis of poultry manure at 425°C, 575°C and 725°C	Lowest sorption capacity of the biochar produced at 425°C, highest Zn and Pb sorption capacity for the biochar produced at 575°C, and highest Cd sorption capacity for the biochar produced at 727°C. Sorption mechanisms are identified as cation exchange, surface complexing, precipitation, and electrostatic interaction.	(Sobik-Szołtysek et al, 2021)
Batch sorption of Cu, solution (20 mL) added to 25 mg biochar	Biochars produced from cow manure pyrolyzed at temperatures from 399°C to 700°C	Highest sorption capacity with the biochar produced at 700°C. Primary mechanisms of Cu sorption identified to be co-precipitation (with formation of copper phosphate and copper carbonate) and cation exchange (with K^+, Ca^{2+} and Mg^{2+}), accounting for 93 to 97% of the adsorption. Secondary mechanisms identified as complexation with oxygen functional groups and cation π interactions.	(Zhang et al, 2021)
Batch sorption of Cr, solution (20 mL)	Biochars prepared from pineapple peels, pyrolyzed at	Removal efficiency of Cr decreased with increasing pyrolyzing temperature. Mechanisms if sorption identified as	(Shakya and Agarwal, 2019)

Table 21.1 *continued*

Experiment	*Biochar preparation*	*Findings*	*Reference*
added to 100 mg biochar	temperatures between 350°C and 650°C	precipitation, complexation with oxygen containing functional groups, electrostatic attraction	
Batch sorption of Pb and Cd, solution (30 mL) added to 0.05 g biochar	Biochars made from tobacco stems pyrolyzed at 400°C, 500°C, 600°C and 700°C	Adsorption of Pb and Cd increased with increasing pyrolysis temperature; highest sorption with biochar at 700°C (Pb: 22 mg g^{-1}, Cd: 19 mg g^{-1}). Mechanisms of sorption hypothesized to be precipitation with inorganic salts.	(Wang et al, 2020)
Batch sorption of Fe, Ni, Cu and Zn; solution (50 mL) added to 0.1 g biochar	Biochars made from date palm wastes (fronds and leaves) pyrolyzed 400°C to 600°C	No influence of pyrolysis on the sorption of Cu, Fe, Ni and Zn.	(Sizirici et al, 2021)

to circumneutral and acidic contaminated substrates, explaining changes in metal and As mobility in pore water (Table 21.2). Various other studies report a soil liming effect of biochars, often resulting from alkaline biochars added to very acidic mine soils. Sizmur et al (2011), for example, highlight an extreme example of an increase in soil pH of more than 4 units when nettle-derived biochar was added to a mine soil (pH 2.7). Other authors note more moderate pH increases of 1–2 units (Jones et al, 2012; Li et al, 2018), whilst column leaching studies have shown the pH effect to be reduced over time as much as ~3 units (Beesley et al, 2022).

Table 21.2

Dissolved organic carbon (DOC) and trace elements in biochars

Fluctuations in dissolved organic carbon (DOC) concentrations have been measured as a consequence of biochar application to soils, and several studies have previously measured the potential co-mobilization of metals in complexes with leached organic materials. In a study utilizing a recirculating column approach, any co-mobilization of Zn induced by DOC from biochar was mitigated by the strong surface binding of this metal with biochar (Beesley et al, 2022). This is likely to be the case for the majority of soil biochar applications, the exception being where some amorphous organic matter is occluded in biochar pores after pyrolysis. The mechanisms for the co-mobilization of As and soluble organic matter are less clear than for metals in the context of biochars. Ternary complex formation between arsenate and ferric iron complexes of ‘humic substance’ extracts could be responsible for the increasing As mobility with increasing DOC (Mikutta and Kretzschmar, 2011). Alternatively, DOC may compete with As directly for retention sites on soil surfaces (Fitz and Wenzel, 2002), resulting in an increase in soluble As with increasing concentrations of DOC (Hartley et al, 2009).

Biochars can be sources of (Chapter 8), or enhance the bioavailability of P (Chapter 16). As phosphate is chemically analogous to As (V), increases in P availability result in the release of As from soil surfaces, into solution and uptake into plants via phosphate ion channels (Meharg and Macnair, 1992).

Table 21.2 *Selected examples detailing pH effects of biochars on heavy metal solubility in pore water, assessed by pot tests*

Experiment	*Soils and biochars*	*Extraction procedure*	*Findings*	*Reported in reference*
Pot trial to determine if biochar is efficient in stabilizing As and Pb	Former mine technosol, very acidic and polluted with As and Pb Hardwood biochar (500°C) applied at 5%	Soil pore water extraction $CaCl_2$ and NH_4NO_3 extraction	Soil pore water pH increased by 3 units $CaCl_2$ extractable As and Pb reduced, by 40% and 42%, respectively NH_4NO_3 extractable Pb reduced by 76% Soil pore water Pb concentration decreased by 96% Biochar effective to stabilize Pb.	(Lebrun et al, 2019)
Pot trial to determine the capacity of biochar to stabilize As and Pb	Former mine technosol, very acidic and polluted with As and Pb Hardwood biochar (500°C) applied at 5%	Soil pore water extraction	Soil pore water pH increased by 2.4 units. Soil pore water Pb concentration decreased by 86% Biochar effective in stabilizing Pb	(Lebrun et al, 2021a)
Pot culture experiment to evaluate the potential impacts of biochar on the bioavailability of multiple metals (Cd, Pb, Cu, and Zn)	Farmland soil (fluvo-aquic soil), with basic pH and contaminated by Pb and Zn Rice huck biochar applied at 0% (control), 1%, 2%, and 3%	DTPA-extractable metals	Biochar application decreased the DTPA-extractable Cd, Pb, Cu, and Zn contents. Biochar effective in stabilizing Pb and Zn	(Wang et al, 2021)

Although arsenate is desorbed from soil surfaces by phosphate (Cao et al, 2003), it is not always available for plant uptake since P and As will compete again for the same root transporter. Therefore, As (V) uptake into plants can be avoided by high concentrations of soluble P (Moreno-Jiménez et al, 2012), but if the soluble fraction of As is not taken up by plants, there is a risk it may leach to surface and groundwaters (Fitz and Wenzel, 2002). On the contrary, phosphate is known to precipitate and sorb Pb (Zeng et al, 2017). Phosphate-rich compounds applied to Pb-contaminated soils have also been found to reduce Pb bioavailability (Miretzky and Fernandez-Cirelli, 2008).

Biochars have heavy metals inherent within their structure, derived from their source material, which may be accumulated and concentrated in ash fractions during pyrolysis. Some biochars exceed European topsoil concentrations, suggesting that they may contribute heavy metal loadings if applied to soils (Table 21.3).

Table 21.3

Table 21.3 *Summary of range of selected heavy metal(loid) concentrations of biochars extracted by acid (aqua-regia)*

Heavy metal (loid)	*Background European topsoil concentrations (mg kg^{-1})*[a]	*Range of concentrations measured in biochars (mg kg^{-1})*	*Source publications*
As	*6*	0.01–9	(Hossain et al, 2010; Bird et al, 2012; Freddo et al, 2012)
Cd	*0.2*	<0.01–8	(Hossain et al, 2010; He et al, 2010; Knowles et al, 2011; Bird et al, 2012; Gascó et al, 2012; Freddo et al, 2012; Van Poucke et al, 2018, 2020)
Cr	*22*	0.02–230	(Hossain et al, 2010; Bird et al, 2012; Freddo et al, 2012; Van Poucke et al, 2018; Van Poucke et al, 2020; Lebrun et al, 2021a)
Cu	*14*	<0.01–2100	(Graber et al, 2010; He et al, 2010; Mankasingh et al, 2011; Knowles et al, 2011; Bird et al, 2012; Gascó et al, 2012; Méndez et al, 2012; Freddo et al, 2012; Van Poucke et al, 2018; Van Poucke et al, 2020; Lebrun et al, 2021a)
Pb	*16*	0.1–196	(Hossain et al, 2010; He et al, 2010; Knowles et al, 2011; Bird et al, 2012; Gascó et al, 2012; Méndez et al, 2012; Freddo et al, 2012; Van Poucke et al, 2018; Van Poucke et al, 2020)
Zn	*52*	0.7–3300	(Graber et al, 2010; He et al, 2010; Mankasingh et al, 2011; Knowles et al, 2011; Bird et al, 2012; Gascó et al, 2012; Méndez et al, 2012; Freddo et al, 2012; Van Poucke et al, 2018; Van Poucke et al, 2020; Lebrun et al, 2021a)

Notes

[a] Source: Lado et al (2008) based on 1588 samples across 26 EU member states; data reported are median values.

Toxicity to plants (phytotoxicity)

The impacts of biochars on soil properties and resultant phytotoxicity are subject to many factors (Chapter 13), such as soil type and local climate conditions (Gao et al, 2020). In a wide-ranging meta-analysis, soil organic matter, pH, and texture were found to be among the key factors to consider when evaluating the effect of biochars on soil parameters that influence plant growth (Arabi et al, 2021). For example, the same biochar was very efficient in immobilizing Pb, promoting vegetation growth, and reducing plant metal uptake in an acidic former mine technosol (Lebrun et al, 2017), while it had no effect at an alkaline former industrial site (Lebrun et al, 2018c). Similarly, biochar application reduced the mobility of Cd, Pb, and Zn when applied on acidic soil but not to basic soil (Álvarez-Rogel et al, 2018). The content of clay and the presence of co-existing ions in the soil were among the factors influencing the effect of biochar on metals and plants (Guo et al, 2020; summarized in Table 21.4).

Table 21.4

Table 21.4 *Selected examples of pot trials where biomass and heavy metal uptake has been measured after soil amendment with biochars alone, or in combination with other organic amendments*

Experiment	*Soil*	*Biochar*	*Findings*	*Reported in reference*
To determine whether biochar can reduce As and Pb toxicity to allow plant establishment	Former mine soil, acidic and highly contaminated with As and Pb	Pinewood biochar added at 2% and 5% (w/w)	Increased *Salix viminalis, Salix alba,* and *Salix purpurea* dry weight with 2% and 5% biochar. Decreased As stem concentration (88%) in *Salix alba* and increased in leaf (41-fold); increased As concentration in the stem of *Salix viminalis*. Increase in leaf Pb concentration of Salix alba and decreased in roots; decreased in Pb leaf and root concentrations of *Salix viminalis*; increased leaf Pb concentration of *Salix purpurea*. Biochar effective at improving soil fertility and plant growth, while stabilizing As and Pb in the root zone	(Lebrun et al, 2017)
To determine the effect of biochar feedstock for the stabilization of As and Pb	Former mine soil, acidic and highly contaminated with As and Pb	Softwood and Pinewood biochars added at 2% and 5% (w/w)	Increase in soil organic matter content and pH. Immobilization of Pb. Increase in *Salix viminalis* and *Populus euramericana* dry weight. Increase in Pb aerial concentrations with biochar. Decrease in As concentration in *Salix viminalis* with pinewood biochar and increase with	(Lebrun et al, 2018b)

Table 21.4 *continued*

Experiment	*Soil*	*Biochar*	*Findings*	*Reported in reference*
			lightwood biochar. Biochar efficient for the assisted phytostabilization of As and Pb in association with poplar or willow. Biochar feedstock important parameter for As and Pb stabilization	
To determine the effect of biochar particle size on the stabilization of As and Pb	Former mine soil, acidic and highly contaminated with As and Pb	Hardwood biochars, with four particle sizes, added at 2% and 5% (w/w)	Increase in soil pH and immobilization of Pb. Increase in *Salix viminalis* dry weight. Fine biochars decreased As stem concentrations, while coarse biochars decreased As leaf concentration. All biochars increased Pb leaf and stem concentration. Biochar improved soil growing conditions and is efficient for As and Pb stabilization when associated with *Salix viminalis*. Fine biochars induce effects more rapidly than coarse biochars	(Lebrun et al, 2018a)
To determine whether biochar, associated with compost, can stabilize As and Pb	Former mine soil, acidic and highly contaminated with As and Pb	Hardwood biochar added at 5% Compost added at 5%	Increased soil organic matter (biochar + compost > biochar > compost). Decreased As availability (biochar = biochar +compost) and Pb availability (biochar > compost = biochar +compost). Increased soil pH and immobilization of Pb. Increased *Salix viminalis* dry weight (biochar = compost = biochar +compost). Decreased As and Pb root concentrations. Biochar,	(Lebrun et al, 2019)

Table 21.4 *continued*

Experiment	*Soil*	*Biochar*	*Findings*	*Reported in reference*
			with or without compost, improved soil conditions and plant growth, and is efficient for As and Pb stabilization	
To determine if the association of biochar with red mud (bauxite mining residue) is efficient for the remediation of As and Pb	Former mine soil, acidic and highly contaminated with As and Pb	Hardwood biochar added at 2% Red mud added at 1%	Increased soil pH, Pb immobilization, and increased *Salix dasyclados* growth. Decreased root Pb concentration and increased leaf and stem Pb concentrations. The association of biochar with red mud is effective for the assisted phytostabilization of As and Pb	(Lebrun et al, 2021d)
To determine if biochar, compost and iron sulfate can stabilize As and Pb	Former mine soil, acidic and highly contaminated with As and Pb	Hardwood biochar added at 5% Compost added at 5% Iron sulfate added at 0.15%	Increased soil C, pH, P and K. Immobilization of Pb. Improved *Agrostis capillaris* growth. The association of the three amendments, with Agrostis, is a good option for the remediation of As and Pb	(Nandillon et al, 2021)
To test whether biochar assist the revegetation of mine spoil	Exposed mine spoil materials from five disused/abandoned mine	Rice husk biochar or wheat straw biochar, added at 5% and 10% (w/w)	More than 99% Zn and 97% Pb adsorbed by the biochars. Increased ryegrass mass and reduced Cd assimilation (2–4 fold), As and Sb concentrations. Decreased Al, Cd, Pb, and Zn mobility. Biochar addition can successfully establish a vegetation cover on mine soil and stabilize metals	(Alhar et al, 2021)
To determine if biochar can reduce pollutant uptake to tomato	Metal contaminated site	Maize stalks biochar added at 5 and 10 t ha^{-1}	Increased N, P, and K availability and decreased pollutant availability. Increased concentration of photosynthetic pigments,	(Almaroai and Eissa, 2020)

Table 21.4 *continued*

Experiment	*Soil*	*Biochar*	*Findings*	*Reported in reference*
			tomato yield, and fruit quality. Decreased Zn, Cu, and Pb concentration in shoots and roots of tomatoes. High doses of biochar decreased Zn, Pb, Cd, and Ni and increased N and K contents in fruits. Biochar application recommended to a metal contaminated soils to improve tomato quality and productivity	
To determine if biochar can restore contaminated soil	Mine waste	Biochar from the distilled waste of lemongrass, added at 1%, 2%, and 4%	Increased soil pH, water holding capacity, organic carbon, microbial biomass C, and nutrient availability. Enhanced palmarosa biomass yield and reduced production of oxidative enzyme (in a dose-dependent manner). The plantation of palmarosa with biochar can restore the soil	(Jain et al, 2020)
To determine the biochar dose allowing soil remediation	Paddy field polluted by wastewater discharged from chemical plant of $ZnSO_4$	Biochar from bamboo powder, added at 1%, 3%, 5%, 7%	Decreased hydrolyzable N and available P. increased soil organic matter, available K, and the activity of urease and polyphenol oxidase. Decreased soil metal concentration. Little effect on *Salix psammophila* growth, except 7% (reduction of growth). The dose of 3% biochar is the best option	(Li et al, 2021)
To evaluate the effect of biochar particle size and application dose	Metal polluted soil	Biochars from oil palm empty fruit bunch, of different	Decreased Pb and Cd solubility. Increased *Brassica juncea* height. Decreased root and shoot	(Samsuri et al, 2020)

Table 21.4 *continued*

Experiment	*Soil*	*Biochar*	*Findings*	*Reported in reference*
		particle sizes, added at 0.5% and 1%	Cd and Pb concentrations. The application of a fine particle size biochar at 1% is the best option to reduce metal transfer in plants	
To determine the influence of different biochars on plant growth and metal uptake	Basic metal contaminated soil. Acidic metal contaminated soil	Biochars from sewage sludge and pruning trees, added at 6%	No influence of biochar on soil pore water pH No durable and significant effect of biochars on metal mobility. No effectiveness of biochar when applied to basic soil Biochar increased soil pore water pH and decreased metal concentration in soil pore water Biochar is a useful option to reduce metal mobility in acidic soil	(Álvarez-Rogel et al, 2018)

Remediation of contaminated sites: lessons from case examples

Principles of soil remediation

We have discussed the main mechanisms by which biochars interact with metal(loid)s in soils, and how these may be directly and indirectly related to biochars' addition to soils. Now we will discuss these factors regarding principles of contaminated land remediation. Contaminated, industrially impacted, mining and urban lands are often characterized by young, poorly developed soils and a scarcity or absence of vegetation cover (Mench et al, 2003). Re-vegetation of contaminated soils is key to their stabilization and remediation (Arienzo et al, 2004; Ruttens et al, 2006), as the presence of a vegetative cover over bare soil reduces the potential for migration of contaminants to proximal waters or inhalation by receptor organisms (Tordoff et al, 2000), as well as the restoration of the natural cycling of organic matter and nutrients. Barriers to re-vegetation include phytotoxic concentrations of heavy metals. In this context, those which plants may not be able to immobilize at the root level (Pulford and Watson, 2003), and poor functionality (organic matter [cycling], nutrient status, structure of soils, water-holding capacity). To overcome these limitations is the general aim of soil remediation using organic amendments (Fangueiro et al, 2018).

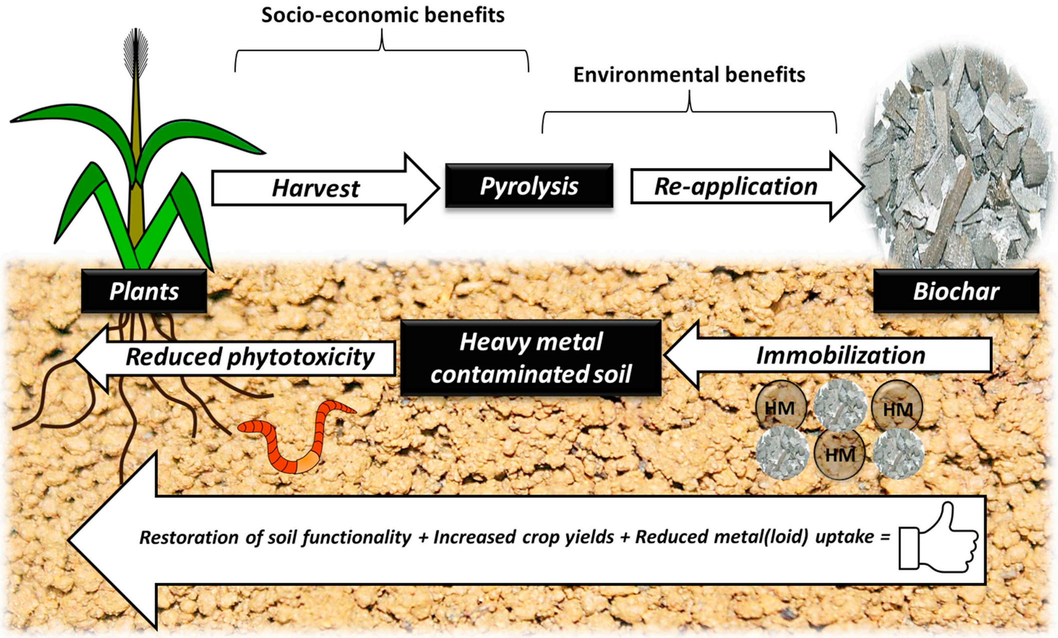

Figure 21.2 *Schematic summary of a remediation system where biochar is deployed to immobilize heavy metals, reduce phytotoxicity, and improve biomass yield. Biomass may be pyrolyzed and re-applied to soils, maintaining a closed system*

Biochars have several well-documented effects on soil health, which should promote functionality and the recovery of degraded land either directly or by indirect mechanisms; liming effects, increased water holding capacity, and improved soil structure, for example (Chapters 13, 16, 20). Many of the documented benefits of biochar addition in this context are only seen when organic or inorganic fertilizers are added together with the biochar amendment, suggesting that biochar alone is often unsuitable as a soil amendment to stimulate re-vegetation (Ye et al, 2020). In fact, some studies report a decrease in plant growth after the amendment of soils with biochar (Beesley et al, 2011, 2013; Li et al, 2021), although others report agronomic benefits when biochar is exclusively added to soils (Shahbaz et al, 2018; Rehman et al, 2019; Almaroai and Eissa, 2020).

Connectivity between (i) biochar efficiency for adjusting the equilibrium between mobile/bioavailable and stable/complexed heavy metals (toxicity); and (ii) soil functionality is the final aspect to consider in biochar application to contaminated sites. This allows an idealized system to be proposed, summarized below (Figure 21.2), where biochar addition to contaminated soils gives multiple benefits to soil quality which, in turn, are beneficial socially and economically.

Fig 21.2

Case examples from acid mines and smelter-impacted soils

Skeletal or weakly structured soils supplemented by waste tailings are common at former mine sites (Wong, 2003) where the original soil horizon sequences may be buried deeply below waste. Point and diffuse pollution of soils are also features of areas previously dominated by industrial processes such as smelting and tanning. As such, limitations exist to revegetation of such soils due to unusual stoichiometry of nutrients to pollutants. In a phytotoxicity test using *Phaseolus vulgaris*, Lomaglio et al (2017) demonstrated the ability of wood biochar to increase soil pH and reduce Cd, Pb, and Zn mobility when applied at 2 and 5% to soil in the vicinity of a former smelter site. In addition, they observed an increase in leaf dry weight at the same application rate, while leaf Cd, stem Pb, and leaf Zn concentrations decreased at 2% and 5% application rate. This demonstrated the potential of such biochar to reduce the toxicity of contaminated soil and thus allow revegetation. Similarly increasing doses of wood biochars were applied to soil impacted by industrial waste disposal. In general, only the higher application rates used here (1% and 2%) had beneficial effects on soil pH, pollutant bioavailability, and wheat growth (Ali et al, 2019). Root and shoot metal uptake decreased following biochar amendment, except for the increase in shoot Cu concentration at 0.5% and 1% biochar doses.

Often, to create functional soils at mine sites, some sort of technical soil (technosol) is created by blending mine spoil with other materials. This was the case in several studies on an As and Pb-rich mine spoil in France. Hardwood biochars, added at 2% and 5% to a mine-impacted soil increased *Populus euramericana* dry weight, raised Pb accumulation in aerial tissues, and lowered leaf As concentration (Lebrun et al, 2021a). In a phytotoxicity experiment, biochar (hardwood, 2% w/w) was mixed with iron sulfate, which increased bean dry weight, without affecting metal(loid) plant accumulation, while biochar alone had no effect (Lebrun et al, 2021b); this example illustrates the intelligent application of iron-based materials with biochars for As contaminated soils. Red mud was also combined with biochar (bamboo, or bark sap oak wood), which increased *Salix triandra* dry weight by 3-fold (leaf), 7-fold (stem), and 15-fold (roots). Lastly, in a study applying biochar, manure, and ocher, in single and combined applications, only the treatments containing manure improved Agrostis growth and reduced As and Pb aerial concentrations (Lebrun et al, 2021c). These studies demonstrate the added value of combining biochar (s) with other amendments that can (i) provide specific metal(loid) sorption capacity (e.g., Fe-rich materials for As); and (ii) supply plant-available nutrients to assist revegetation (e.g., manures).

A similar strategy was employed to revegetate Cu-rich mine soil in Spain (Forján et al, 2018a). Mesocosms containing biochar/compost and biochar/technosol ratios applied to soil was 4:11 in both cases, to reflect as closely as possible its application in the field. Furthermore, the treatments were applied on the first 0.15–0.2 m of soil as this would be the way they would be applied. Additionally, seeds of *Brassica juncea* L. (phytoremediator species) were planted and pore water samples were collected at three different depths of the cylinders. The Cu concentrations decreased in pore water samples collected for 11 months, demonstrating Cu stabilization in the settling pond soil with the addition of biochar compost. The main factors favoring the decrease of available Cu concentrations were the increase in pH, the increase of organic carbon content, and the correction of cation exchange capacity (Forján et al, 2018a). In addition, specific surface area and functional groups of the biochar could have a positive effect in reducing the available Cu concentrations (Forján et al, 2018a). On the other hand, both treatments besides increasing carbon content also contributed to a rise in total soil nitrogen, improved nutrient retention, and contributed to soil restructuring. Thus, the treatments improved the physicochemical properties of the soil and favored the establishment of vegetation (Forján et al, 2018b). The biochar-compost treatment therefore improved both immobilization of Cu and plant growth (Forján et al, 2018c). *Brassica juncea* L. had a clear phytostabilizing activity over the Cu, despite not having phytoextraction capacity according to the obtained translocation factor (TF) and transfer coefficient (TC). At low TF values, Cu was not translocated from the root to the shoot, while it was fixed in the roots. This phytostabilization technique proved most appropriate to immobilize metals in mining sites, resulting in less exposure to this toxic element by livestock, wildlife, and human health (Forján et al, 2018b).

The particular issue of calcareous soils

Studies detailing the deployment of biochars into calcareous soils are scarcer than into acidic soils. It is important to remember that association with the exchangeable or carbonate fraction may reduce mobility under specific conditions of alkalinity. However, a reduction in pH, though slight, may cause the release of metals, and as such, metals in these associations are considered potentially mobile.

In a study carried out in a mining region in central Mexico, sediments presented geochemical characteristics generally conducive with limiting metal mobility, including neutral pH, high organic matter content, and very calcareous conditions (Mitchell et al, 2016). While the impact that each of these characteristics has on metal mobility depends principally on pH, a general prevalence of metals associated with the carbonate fraction can be expected in soils with neutral to alkaline pH, which was confirmed through sequential extraction. These associations with the carbonate fractions are considered temporary as changes in physicochemical characteristics, especially pH, can easily remobilize associated metals.

To evaluate the effect of the amendment, biochar produced from sewage sludge and the non-pyrolyzed source material were applied to the affected sediments. Each week, for 28 days, metals were leached with $CaCl_2$ 0.01 M at pH 5.5, simulating typical conditions, and pH 3.5, simulating more extreme conditions (Houben et al, 2013). Notably, non-pyrolyzed sewage sludge was more effective at reducing metal(loid) mobility at pH 5.5, while biochar was more effective at pH 3.5. Sequential extraction confirmed an increase in the association of Pb and Cd to stable Fe, Mn, and organic matter fractions and a decrease in association with the mobile carbonate fraction (Mitchell et al, 2020). Zinc mobility demonstrates different sorption characteristics when found in complex metal matrices and, in the highlighted study, there were no significant differences in Zn mobility when leached at pH 3.5 or pH 5.5. It is reasonable to assume that the extraction at a more acidic pH, results in a predominance of metal-organic matter associations instead of precipitation, which may occur at higher pH. Sequential extraction showed a reduction of Zn associated with the potentially mobile exchangeable and carbonate-bound fractions. There was an increase in Zn association with more stable fractions in both cases, though association with the organic matter fraction was predominant in sediments amended with unpyrolyzed sludge, likely due to the high affinity of Zn for the major complexing agents found in unmodified organic matter including oxygenated carboxylic and amino groups. On the other hand, associations with the Fe and Mn oxide increased when amended with biochar, likely due to the decreased presence of these functional groups but a proportionate increase of stable Mn oxide sites. Thus, even in calcareous soils and sediments with an inherently elevated buffer capacity, amendment with biochar could reduce metal leachability in the long term.

Specific enhancements of biochars

In the context of the remediation of soils (Chapter 27), improvements or amendments to biochar formulations, such as by co-composting with other organic materials (Chapter 26) have been shown to favorably adjust soil physical-chemical characteristics in metal-contaminated soils (Teodoro et al, 2020). Iron oxides (FeOx) and other metal oxides (Al, Mn, etc.) are effective binding surfaces for metals and metalloids such as As, Hg, Se, Cr, Pb, etc., and are used in the remediation of heavy metal contaminated substrates (Warren et al, 2003; Waychunas et al, 2005). Arsenic is widely known to be immobilized by Fe-rich materials as they provide anion exchange sites (Masscheleyn et al, 1991), so optimizing biochar for metal and As retention may be possible by modifying its characteristics during production or pre-application (Dixit and Hering, 2003) and Fe oxide impregnated sorbents have been widely applied to contaminated waters (Reed et al, 2000; Vaughan and Reed, 2005). Soaking the source material with Fe chloride solution before pyrolysis entrains the Fe oxide into the biochar structure (Chen et al, 2011). Alternatively, the biochar may be soaked in a Fe solution after pyrolysis (Muñiz et al, 2009; Lebrun et al, 2018a). The cost of producing these biochars will be greater than unmodified biochar, so they may only be suitable for specific small-scale applications.

Biochar applications to urban agriculture sites

The application of biochars on an experimental basis to urban agriculture sites has been limited, with previous studies highlighting mixed results (Barrow, 2012; Werner et al, 2019). The potential role of biochar within urban farming practices highlights a smaller scale, and very targeted application of biochars (Song et al, 2020); many urban agriculture sites consist of small pockets of land, and diverse history and pollution legacy (Dennis et al, 2020). Here, biochar presents an opportunity to produce a soil amendment in situ and at the point of usage. With land often at a premium in cities, approaches such as retrofitting urban rooftop farming have gained traction in recent years (Hardman and Larkham, 2014). An obvious and prohibitive barrier to this has been the mass-to-volume ratio of traditional (soil-based) substrates (Orsini et al, 2017), especially when saturated or semi-saturated. The use of biochar on rooftops may be driven by a need for lighter substrates and improved plant-available water (Cao et al, 2014).

Conclusions and recommendations for biochar deployment

Biochars can offer several advantages alone or in combination with other amendments during heavy metal remediation of soils because:

- Biochars have a greater surface area than soils to which they are added and some have higher CEC meaning they are capable of sorbing high concentrations of heavy metals, such as Cd and Zn from the soils they amend. This is especially the case in soils low in organic matter with intrinsically low CEC.

- Biochars are more persistent in soils for longer periods than other commonly applied soil amendments, such as composts and sludges, and may not induce as great deal of co-mobilization effect between easily mineralizable organic fractions and heavy metals. Biochars can also raise the pH of soils, making some nutrients more available to plants, immobilizing some heavy metals, and liming acid soils.
- Biochars can assist in the re-vegetation of some contaminated soils by reducing phytotoxicity and improving the germination of seeds.
- Biochars may be effective at immobilizing metal(loid)s in acidic and calcareous soils, though studies on the latter are scarce.

Remediation strategies for industrial, mine, or urban soils could include biochars for reducing the leaching of heavy metals, decreasing the phytotoxicity of substrates, and assisting revegetation. In the case of As-contaminated sites, and especially where there is a potential that food crops may be cultivated (for example urban allotment sites), a greater degree of caution should be exercised not only in whether or not to apply biochar, but also in what method of application and how much should be applied. Some biochars also contain elevated concentrations of heavy metals due to their source material. It must also be remembered that most biochars appear sub-optimal as fertilizers if applied alone, so there may be a need to combine them with materials containing available nutrients; co-composting with other organic materials is one such option. At very heavily contaminated and denuded sites, such as former mine areas, particularly where there are surface leachates of heavy metals and unconsolidated soils and wastes, biochars may be useful to restrict the wider impact of contamination beyond site boundaries. By the same principle, after a surface pollution incident, biochars may also be used to reduce the spread of contaminants to groundwater. Combination with other organic materials is likely to be required for effective phytostabilization and remediation. At old industrial sites, there may be sufficient native soil remaining, and remaining nutrients so that biochars can be applied alone to contamination hotspots to restart natural plant successions. In all cases, an intelligent approach should be taken to biochar application to land after some data has been gathered about the specific soil characteristics, and heavy metals present in elevated concentrations, preferably their bioavailability and their wider dispersal.

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