



Stabilization of hard rock mines tailings with organic amendments: pore water quality control and revegetation – a review

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ABSTRACT

Organic amendments aided with vegetation are considered a promising prevention approach for the stabilization of metal-contaminated tailings. However, the inconsistency in the performance of different amendments and their effects on plants growth indicate that further studies are still required. To better select the appropriate organic amendments and identify future research avenues for mine tailings stabilization, this critical review makes a preliminary compilation of available knowledge on organic amendments and their reported performance. To this end, data were collected from several review papers and case studies, with a particular focus on the evolution of pore water quality and plant phytostabilization abilities. The screening of the most promising materials was then carried out according to whether metallic elements were mobilized/immobilized from pore water, sequestered into rhizosphere or plant aboveground parts. Results showed that mixture of organic and inorganic materials are more efficient than organics alone. Amendments combining mature and composted animal manures with inorganic materials would be more promising. Conversely, fresh compost and biosolids could enhance metals release in pore water and, possibly, the transfer in plants aerial parts. Finally, biochars could be efficient if mixed with raw organic amendments but the effect on vegetation still needs to be evaluated. Further studies should focus on amendment-plant-microbes interactions and the long-term stability of organic amendments (>10-20 years).

Keywords: Revegetation; Mill tailings; Biochar; Manure; Compost; Trace metals and metalloids; Pore water chemistry; Element speciation; Plant uptake

1. Introduction

Sulfide-bearing minerals in tailings are chemically instable, when exposed to weathering, and generate low-quality pore water and contaminated mine drainage which may adversely impact the surroundings [1]. To prevent, limit or mitigate the environmental impacts, stabilization measures are required. The main objective of stabilization approaches is to prevent the generation of acid mine drainage. Prevention measures can involve the use of covers (water and organic/inorganic

materials), with/without vegetation for a control of water and/or oxygen access to the reactive waste, and the desulfurization of sulfide-bearing tailings prior to storage [2,3]. In the case of weathered and highly contaminated tailings, additional treatment of the contaminated pore water is often necessary because it may take a number of years before being totally discharged [4,5]. In closed and abandoned mine sites, passive treatment is used, but the long-term performance is warranted by early implementation [6]. Alternatively, the use of organic materials, as amendments, combined with revegetation (phytostabilization) seems to be a promising stabilization approach

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for the stabilization of metal-contaminated tailings. This last approach offers the advantage of a simultaneous physical (limitation of wind and water erosion) and chemical (acid neutralization, metals/metalloids immobilization) stabilization. The mixing of tailings with organic amendments leads to the improvement of their physicochemical (water-holding, porosity, nutrition) and biological properties (vegetation development and microbial proliferation) [7–9]. In addition, the phytostabilization, which consists of establishing vegetative covers on the surface of the amended tailings, is used to prevent direct exposure to wind, water, human and animal contact, and to limit the mobility of contaminants through their immobilization within the rhizosphere (rhizoremediation) or accumulation by roots [8,10–12]. Revegetation also improves esthetic of mine tailings [13], but should be tolerant to the presence of phytoavailable salts and metals in pore water [10,13]. In the same time, organic amendments can be a major source of contaminants (metallic elements, pathogens and toxins) and their performances regarding mobilization/immobilization of metallic elements in pore water are variable depending on the type (fresh vs. mature), source (industrial vs. raw), physicochemical properties, durability (decomposition rate), application mode (alone or in mixture and dosage), tailings characteristics (highly contaminated vs. slightly contaminated, fresh vs. weathered) as well as plant species [7–10,14–16]. As for the plants, they can influence the physicochemical and microbial characteristics of soil and the redox conditions of the rhizosphere through root exudates [8]. Thereby, speciation of metallic elements in pore water and their bioavailability may change after application of amendment and revegetation [7]. To better select appropriate materials and plant species for the stabilization of metal-contaminated mine tailings, this critical review makes a preliminary inventory of organic amendments and their performance, and identifies future research needs for an efficient use.

2. Method

Data compiled from review papers (18) and case studies (98) were collected, with a focus on pore water quality and plant phytostabilization abilities. Case studies compile results from laboratory [15,17–19], greenhouse [20–23], and field experiments [24–27]. The key performance of the tailings stabilization was evaluated by the pore water quality and phytostabilization. Pore water quality was monitored through the evolution of physicochemical parameters, including pH, electrical conductivity (EC), oxydoreduction potential (ORP), water-holding capacity, cationic exchange capacity (CEC), concentrations of total/dissolved organic carbon (TOC/DOC), nutrients (Ca, Mg, N, P, K), organic matter (OM) and metals/metalloids (including trace elements) (Fig. 1). Phytostabilization failure or success (generally in field conditions) is evaluated through plant aerial growth (comprising germination), biomass production and bioaccumulation (metallic elements concentration in shoot/root tissues), as well as mid-term evolution, that is, 0–5 years (plant self-sustaining and toxicity).

Following data synthesis, the sorting of the most promising organic amendments was undertaken depending on whether particular metallic elements were mobilized/immobilized from pore water through speciation change (not including microbial mediation), or sequestered into either rhizosphere

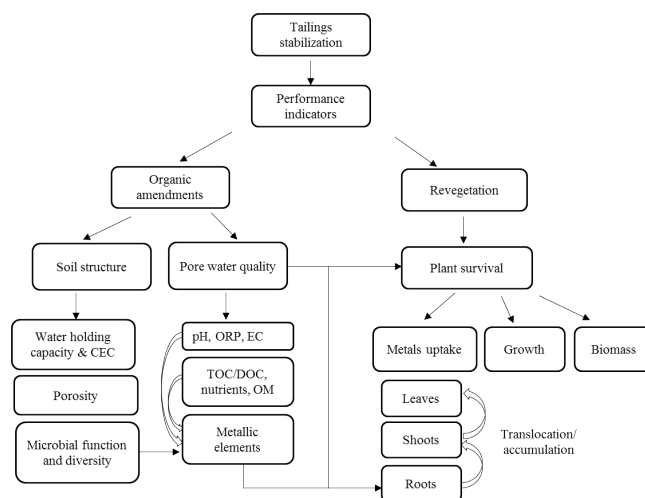


Fig. 1. Key performance indicators of tailings stabilization success by application of organic amendments and revegetation.

or plant aboveground parts. Advantages and limits of organic amendments (alone or in mixture between organic amendments of the same or different nature, with/without addition of inorganic materials) used for the stabilization of metal-contaminated mine tailings were also recorded.

3. Results and discussion

Tailings are fine-grained (<2 mm) materials obtained after extraction of valuable metals/minerals from metalliferous ores [28]. They lack OM, nutrients, soil organisms, physical structure and have low hydraulic conductivity, that limit vegetation development [12,13,20,28,29]. Tailings pore water can exhibit extremely low to neutral pH and high EC, as well as slight to high concentrations of contaminants (including metallic elements) [20,22,27]. Organic material influences the evolution of the physicochemical characteristics of tailings pore water and the speciation of metallic elements which in turn has impact on plant development.

3.1. Influence of organic amendments on physicochemical characteristics of tailings

Inventory of the organic amendments presently tested for tailings stabilization includes composts (green wastes, municipal solid waste, olive mill waste, sewage sludge and spent mushroom), biosolids (sewage sludge, food wastes, sanitary wastes and anaerobic digestate), manures (cow, cattle, pig and poultry), biochars (rice straw, hardwood, oak tree, fir tree, pruning residues and manure pellets), slurry (pig and cattle) and peat (Table 1) [7–9,30,31]. They are used alone, in mixture with organic amendments of the same/different sources [8,21,26,32] or combined with inorganic (alkaline) materials (hydrated lime/limestone, red mud, marble waste, zeolite) (Table 2) [9,15,33–37]. A rough quantification of biowastes worldwide, either used for compost production or as raw materials, showed 0.08–25 ($\times 10^6$) t/year of produced biosolids, 8.4–225 ($\times 10^6$) t/year of animal and poultry manures, 2–596 ($\times 10^6$) t/year of municipal solid waste and 1.4–1,633 ($\times 10^6$) t/year of plant residues [38].

Table 1
Selected references on the advantages and limits of single organic amendment with the support of vegetation for mine tailings stabilization

Amendments	Contaminants	Dosage	Vegetation	Advantages	Limits	References
Compost						
Municipal solid waste (pH 7.28 ± 0.03)	As, Cu, Pb, Zn (pH = 2.91)	60 % (v/v)	<i>Agrostis capillaris</i> L.	<ul style="list-style-type: none"> • Increase of pH (7.29) • Decrease of As, Cu, Pb and Zn in soil pore water 	<ul style="list-style-type: none"> • Higher Zn uptake • High foliar concentration of Pb • Significant accumulation of Ni at the aboveground biomass 	[82]
Municipal solid waste (pH 7.3)	Zn, Pb, Cd (pH = 6.1)	5%	<i>Medicago sativa</i> L. (alfalfa)	<ul style="list-style-type: none"> • High Zn and Cd adsorption capacity • Improvement of dehydrogenase activity • Low phytotoxic effect 	<ul style="list-style-type: none"> • Decrease of Zn and Cd adsorption capacity 	[46]
Municipal solid waste + bark chippings (pH 6.18 ± 0.04)	Al, Mn, Cu, Zn, Ni (pH = 3.06)	250 kg/t _{dw}	<i>Salix</i> spp. (<i>Salix caprea</i> Maurerbach and <i>S. viminalis</i>), <i>Populus nigra</i> L.	<ul style="list-style-type: none"> • pH increase (6.5 after 3 years) • Increase in soil enzyme activities • Maximum height of plants after 2 years 	<ul style="list-style-type: none"> • Increase of total concentration of Mn, Pb and Zn in the mixture? • High Fe and Mn concentrations in leaves 	[68]
Green waste (pH 8.11)	As, Cu, Pb, Zn (pH = 2.91)	60% (v/v)	<i>Agrostis capillaris</i> L.	<ul style="list-style-type: none"> • Increase of pH (6.83) • Decrease of Cd, Cu, Pb and Zn concentrations in plant shoots 	<ul style="list-style-type: none"> • No increase of biomass • Stimulation of As release in pore water 	[82]
Green waste (pH 6.7 ± 0.01)	Trace elements (As, Mn, Cu, Ni, Pb, Zn) (pH = 7.9)	13% _{dw}	<i>Larix laricina</i> (Du Roi) K. Koch, <i>Pinus banksiana</i> Lamb., <i>Salix viminalis</i> L. and <i>P. x canadensis</i> Moench x <i>P. maximowiczii</i> A. Henry	<ul style="list-style-type: none"> • Improvement of P nutrient for tree • Allowed survival of trees compared with bare tailings 	<ul style="list-style-type: none"> • Poor plant development, especially rooting 	[90]
Greenwaste + dairy manure (pH 9.3 ± 0.3)	As, Pb, Cu, Cd, Cr, Fe, Zn (pH = 2.5)	228 – 456 t/ha	<i>Buchloe dactyloides</i> (Nutt.) J.T. Columbus, <i>Festuca arizonica</i> V., <i>Atriplex lentiformis</i> (Torr.), <i>Cercocarpus montanus</i> Raf., <i>Prosopis juliflora</i> (Sw.), <i>Acacia greggii</i> G.	<ul style="list-style-type: none"> • Low metals concentration in plant shoot 	<ul style="list-style-type: none"> • Small amount growth of <i>Festuca arizonica</i> V., <i>Cercocarpus montanus</i> Raf., <i>Prosopis juliflora</i> Torr. var. <i>glandulosa</i>, <i>Acacia greggii</i> G. at dosage < 342 t/ha 	[47]
Food waste (pH = 8.3 ± 0.28)	Pb, Zn, Cd, Cu (pH=6.11)	25% _{dw}	<i>Phaseolus max</i> L., <i>Zea mays</i> L., <i>Capsicum annuum</i> L., <i>Cenchrus ciliaris</i> L., <i>Sorghum bicolor</i> L., <i>Hordeum vulgare</i> L.	<ul style="list-style-type: none"> • High N mineralization • High dehydrogenase activity • Low Zn mobility 	<ul style="list-style-type: none"> • Leaching of inorganic NO₃-N 	[67]

(Continued)

Table 1 *Continued*

Amendments	Contaminants	Dosage	Vegetation	Advantages	Limits	References
Yard waste (pH 5.8)	Cd, Pb, Zn (pH=7.4)	90 Mt/ha	-	<ul style="list-style-type: none"> Efficient for Zn and Pb immobilization 	<ul style="list-style-type: none"> Increase Zn pore water Do not increase TOC 	[58]
Catering waste + paper waste (pH 7.80±0.16)	As, Cu, Pb, Zn (pH=2.91)	60 % (v/v)	<i>Agrostis capillaris</i> L.	<ul style="list-style-type: none"> Increase of pH (6.94) Increase of biomass Decrease of As, Cu, Pb, Zn in soil pore water 	<ul style="list-style-type: none"> Leaching of water soluble-C High foliar Pb concentration Stimulation of As release in pore water Significant accumulation of Ni in the aboveground biomass 	[82]
Cattle manure (pH 7.1)	Cd, Pb, Zn (pH=7.4)	90 Mt/ha	-	<ul style="list-style-type: none"> Efficient for Pb immobilization 	<ul style="list-style-type: none"> Do not increase TOC Leaching of water soluble-C 	[58]
Poultry manure + chaff (pH 8.17)	Cd (pH=6.5)	0-216 t/ha	<i>Triticum aestivum</i> L.	<ul style="list-style-type: none"> Significant increase of pH at high dose (216 t/ha, pH=7.46) Increase of OM in soil Decrease in Cd concentration (up to 76%) in stems (dose 27-54 t/ha) Optimal dose: 54 t/ha 	<ul style="list-style-type: none"> Low decrease of Cd concentration in stems at high dose (>108 t/ha) Risk of phytotoxicity at high dose (108-216 t/ha) 	[64]
Biochar						
Pruning residues [ROM], Fir tree [ABE], Manure+ fir tree [MAN] (pH 7.65-10.2; T=500°C)	Fe, Cr, Pb, Ti, Zn (pH = 7.76)	1.5% _{dw} 3% _{dw}	<i>Anthyllis vulneraria</i> , subsp. <i>polyphylla</i> (Dc.) Nyman, <i>Nocca rotundifolium</i> (L.) Moench subsp. <i>cepaefolium</i> , <i>Poa alpina</i> L. subsp. <i>alpina</i> (L.)	<ul style="list-style-type: none"> Best biochar: MAN (3%) Great Pb reduction with MAN and ROM (3%) ABE and MAN reduce Cd concentration 	<ul style="list-style-type: none"> High metals concentration (Cd, Pb, Zn) in shoots with addition of ABE > 1.5% High translocation factor of <i>A. vulneraria</i> L. and <i>N. rotundifolium</i> L. with addition of ABE Higher ash content in ABE and MAN 	[30,31]
Beetle-killed lodgepole pine (<i>Pinus contorta</i>) (pH 9.40 ± 0.19; T = 500°C-700°C)	Al, As, Cd, Cu, Fe, Pb, S, Zn (pH = 3.33)	0%-30% (v/v)	-	<ul style="list-style-type: none"> Increase in moisture content of soil Decrease of Al, Cd, Cu and Fe in soil pore water 	<ul style="list-style-type: none"> Low OM in soil Slight increase of pore water pH (3.63) Increase of total dissolved solids in soil pore water No significant effect on As or Pb concentrations in soil pore water Increase of Cd (80%) and Zn (91%) concentration in soil pore water Low organic-C availability and low microbial activity Dose of 30% might not be enough 	[110]

(Continued)

Table 1 Continued

Amendments	Contaminants	Dosage	Vegetation	Advantages	Limits	References
Jarrah, pine wood chips (pH 9.43 ± 0.03; T° = 700°C)	Cu, Zn	10% (v/v)	–	<ul style="list-style-type: none"> Jarrah biochar had higher Cu and Zn adsorption Higher Cu adsorption with jarrah-biochar and Zn adsorption with pine biochar in pore water 	<ul style="list-style-type: none"> Low efficiency in the presence of high sulfate concentration 	[76]
Pig manure (pH = 10.52; T° = 500°C)	As, Cd, Pb, Zn (pH = 2.82)	10 g/kg, 20 g/kg	<i>Piptatherum miliaceum</i> (L.) Coss.	<ul style="list-style-type: none"> Increase of pH (7–8) Increase of total N Decrease of the exchangeable fraction of Cd, Zn and As Dosage of biochar did not affect metal(loids) uptake by plants Low translocation of metals from roots to aerial parts of plant Increase of soil OC, N 	<ul style="list-style-type: none"> The presence of plant increased 20% of EC Low soluble organic-C 	[111]
Municipal solid waste, crop residue, pig manure (pH = 7.78–10.77; T° = 500°C)	Cd, Cu, Pb, Zn (pH = 2.82)	20 g/kg	–	<ul style="list-style-type: none"> Increase of soil pH and decrease of bioavailable metals Greater decrease of bioavailable metal concentrations with lodgepole pine biochar (recommended dose: 5%–10%) 	<ul style="list-style-type: none"> Low labile and water soluble organic compounds Increase of N₂O emissions with crop residue biochar 	[37]
Lodgepole pine, tamarisk (pH = 9.1–10.4; 1st stage: T° = 500°C–700°C; 2nd stage: T° = 300°C–500°C)	Cd, Cu, Zn (pH = 5.12–5.33)	0%–15 % (w/w)	–	<ul style="list-style-type: none"> Increase of soil pH and improvement of mechanical resistance and water-holding capacity 	<ul style="list-style-type: none"> Increasing dose amplified Cu in the Fe/Mn oxyhydroxide phase Higher increase of soil pH with tamarisk biochar than lodgepole pine biochar 	[112]
Pine wood (pH = 7.8; T° = 650°C)	As, Fe, Mn, Cu, S (pH = 7.7)	10% (w/w)	<i>Iseilema vaginiflorum</i> L., <i>Acacia chisholmii</i> F.M. Bailey	<ul style="list-style-type: none"> Increase of plant growth, elemental concentrations in root zones Low water soluble Cu and Mn in tailings Low Cu level in shoots of plants 	<ul style="list-style-type: none"> No change of tailings pH Lack of nutrients in treated tailings Little effect on enzyme activities and low microbial basal respiration High S concentrations in roots and shoots of <i>I. vaginiflorum</i> 	[113]
Raw manures						
Cattle (aged; pH = 6.3)	Cd, Pb, Zn (pH = 7.4)	90 Mt/ha	–	<ul style="list-style-type: none"> Increase of TOC Increase soil pH (8) 	<ul style="list-style-type: none"> Increase of Zn and Pb in pore water 	[58]

(Continued)

Table 1 (Continued)

Amendments	Contaminants	Dosage	Vegetation	Advantages	Limits	References
Poultry (mature; pH = 7.9)	Pb, Zn (pH = 6.1)	150 kg/ha	<i>Festuca rubra</i> L., <i>Lactuca sativa</i> L.	<ul style="list-style-type: none"> • Decrease of Pb bioavailability • High plant biomass • Lower Pb and Zn concentrations in plant shoot (<i>F. rubra</i> L.) 	<ul style="list-style-type: none"> • Shoot Pb (50 times) and Zn (10 times) concentrations in plants: higher than in grass growing in non-metal contaminated sites 	[24]
Pig (pH = 8.48 ± 0.23)	As, Cd, Pb, Zn (pH = 3.55; pH = 7.44)	170 kg/ha _{DM}	<i>Piptatherum miliaceum</i> (L.) Coss., <i>Sonchus tenerrimus</i> L., <i>Dittrichia viscosa</i> (L.) Greuter, <i>Fagonia cretica</i> L., <i>Zygophyllum fabago</i> L.	<ul style="list-style-type: none"> • Increase of pH (~7.5 for acidic tailings and ~8.3 for neutral tailings) • Decrease of EC • Increase of basal soil respiration • Decrease of the soluble fractions of metals except for As • Higher vegetation colonization 	<ul style="list-style-type: none"> • Decrease of soil organic-C over time • Increase of soluble As (~90%) 	[87]
Others						
Biosolids (pH = 6.20)	Fe, Cu, Zn, SO ₄ (pH = 7.98)	100 t/ha, 200 t/ha	<i>Lolium perenne</i> var Nui, <i>Polygonum australis</i> Brongn.	<ul style="list-style-type: none"> • Increase of DOC (1-2 order of magnitude higher) • Increase in microbial basal respiration • Long term N availability 	<ul style="list-style-type: none"> • High total dissolved Cu in pore water • Increase of EC 	[34]
Peat (pH = 5.0)	Zn, Pb, Cd (pH = 6.1)	5%	<i>Medicago sativa</i> L. (alfalfa)	<ul style="list-style-type: none"> • High OM contents • No increase of soil EC 	<ul style="list-style-type: none"> • Recommended dosage < 200 t/ha • High Cu concentration in shoots • Decrease pH 	[46]
Sewage sludge (pH = 7.8)	Al, As, Fe, Mn, Cu, Cr, Co, Ni, Mo, Pb, Zn (pH = 6.6)	6.5 kg _{DM} /m ² (cover of 20 cm)	<i>Hordeum vulgare</i> L., <i>Festuca rubra</i> L.	<ul style="list-style-type: none"> • Low phytotoxicity effects • Low soluble As and Cd • Tolerable level of metals for cattle in <i>F. rubra</i> L. 	<ul style="list-style-type: none"> • Ineffective for Zn and Cd immobilization • Low adsorption capacity • Decrease of pH (4.8) • Increase of Al, Pb, Cd, Zn during growing season • Poor establishment of vegetation • Mn in barley (<i>H. vulgare</i>) straw and Zn in barley grain • High content of Al, Cu, Zn, Pb, As and Cr in shoot of <i>F. rubra</i> L. 	[44]
Sewage sludge (pH = 7.8)	Al, Cu, Mn, Ni, Zn, Cd, Pb (pH = 3.3-3.8)	33.3 g _{DM} /kg _{DM}	-	<ul style="list-style-type: none"> • High dissolved organic matter (DOM) 	<ul style="list-style-type: none"> • Slight buffering effect (final pH = 3.8) • Leaching of all metals 	[17]
Paper mill sludge (pH = 8.2)	Cu, Pb, Zn (pH = 4.1)	30 % (w/w)	<i>Lupinus albus</i> L.	<ul style="list-style-type: none"> • Decrease of mobile Pb, Cu and Zn in soil (high Zn immobilization) • Decrease in shoot Pb and Zn concentrations 	<ul style="list-style-type: none"> • High metal content of the amendment 	[114]

(Continued)

Table 2
Selected references on the advantages and limits of (organic + organic) or (organic + inorganic) amendments combined with vegetation for mine tailings stabilization

Amendments	Contaminants	Dosage	Vegetation	Advantages	Limits	References
Organic + organic Biochar (holm oak tree)+ compost (rabbit and horse manure, pruning residues, seaweeds and fruit wastes) (pH = 9.91 ± 0.26)	Cu, Ni, Pb, Zn (pH = 2.96)	20% _{dw} -80% _{dw}	<i>Brassica juncea</i> L.	<ul style="list-style-type: none"> • Decrease of Cu concentration in soil • Effective bound of Cu • Effective dosage: 40% • Low solubility of Pb in soil • Decrease of Cu, Ni and Pb mobility 	<ul style="list-style-type: none"> • Increase of pseudo total Zn concentration in soil 	[21]
Biochar (raw hardwood; pH 6.96) + compost (industrial; pH = 7.2)	Ni, Zn (pH = 6.5)	0%-20% (w/w) + 0%-40% (w/w)	Red fescue and ryegrass	<ul style="list-style-type: none"> • Decrease in total concentration of 90%-98% Ni and 83%-97% Zn in pore water • 5% biochar+ 5% compost: minimum dosage for germination and plant growth • Increase of stable fraction of metals • Absence of exchangeable fraction of metals 	<ul style="list-style-type: none"> • High dosage of biochar may lead to immobilization of available nutrients and failure of germination 	[25]
Biochar (biomass from <i>Acacia dealbata</i> ; pH = 9.44 ± 0.1) + waste (sewage sludge, sludge from an aluminum plant, ash, food industry wastes, sands; pH = 5.54 ± 0.1)	Cu, Pb, Zn (pH < 3)	97% (w/w) + 3% (w/w) (as mixture: 20%-60% w/w)	-	<ul style="list-style-type: none"> • Slight increase of pH (~5.4) • Optimal dosage: >40% • Sorption of Pb from dosage of 20% • Sorption of Zn and Cu at dosage >40% 	<ul style="list-style-type: none"> • Low sorption of Zn • Lower sorption for a dosage of 20% 	[74]
Biochar (<i>Quercus ilex</i> wood; pH = 9.9 ± 0.02) + compost (horse rabbit manure, grass cuttings, fruit, seaweed; pH = 6.47 ± 0.02)	Al, Cu, Pb, Ni, Zn (pH = 2.73)	4% + 11%	<i>Brassica juncea</i> L.	<ul style="list-style-type: none"> • Increase of soil pH and CEC • High biomass 	<ul style="list-style-type: none"> • Increase of Mn concentration in soil 	[23]
Manure (goat; pH = 7.92) + olive residue (pH = 5.71)	Fe, Cu, Zn, SO ₄ (pH = 7.98)	67 + 96 t/ha	<i>Lolium perenne</i> var Nui, <i>Polygonum australis</i> Brongn.	<ul style="list-style-type: none"> • Increase of DOC (1-2 order of magnitude higher) • Long term N availability 	<ul style="list-style-type: none"> • Increase of total dissolved Cu in pore water • Increase of EC 	[34]

(Continued)

Table 2 *Continued*

Amendments	Contaminants	Dosage	Vegetation	Advantages	Limits	References
Manure (poultry) + sludge (paper mill) (pH = 7.7)	Cd, Pb, Zn (pH = 6.1)	2:1 (v/v) (150 kg/ha)	<i>Festuca rubra</i> L., <i>Lactuca sativa</i> L.	<ul style="list-style-type: none"> Improvement of soil physicochemical High value of <i>F. rubra</i> L. biomass Low phytotoxicity Lower shoot metal (Pb and Zn) concentrations of <i>F. rubra</i> L. Better growth of <i>L. laricina</i> (Du Roi) K. Koch 	<ul style="list-style-type: none"> Possible leaching of labile Zn without vegetation 	[24]
Paper mill sludge + organic NPK fertilizer	As, Cu, cyanide (pH = 6.4–8.1)	1,400 kg/ha	<i>Pinus banksiana</i> Lamb., <i>Picea mariana</i> (Mill.) Britton, Sterns & Poggenb., <i>Alnus viridis</i> ssp. <i>crispa</i> , <i>Cornus sericea</i> , <i>Salix</i> L., <i>Larix laricina</i> (Du Roi) K. Koch, <i>Abies</i> Mill., <i>Echinacea purpurea</i> (L.) Moench	<ul style="list-style-type: none"> Higher soil nutrients with 10% amendment Optimal dose: 10% Decrease of Ni and TI concentration in pore water 	<ul style="list-style-type: none"> No increase of OM of the tailings Potential leaching of nutrients 	[66]
Peat + biosolids (municipal)	SO ₄ , S ₂ O ₃ , Zn, Fe, Mn, Sb, As, TI (pH = 7.65–8.53)	2.5% (v/v) + 2.5% (v/v)	–	<ul style="list-style-type: none"> Increase of pore water alkalinity Removal of Sb in soil pore water 	<ul style="list-style-type: none"> Lower sulfate reducing bacteria in amended tailings Enrichment of SO₄ in soil pore water Increase of Fe, Mn and As in soil pore water and lower removal of Zn, Sb and TI 	[78]
Peat + spent-brewing grain + biosolids (municipal)	SO ₄ , S ₂ O ₃ , Zn, Fe, Mn, Sb, As, TI (pH = 8.0)	2.5%–5% + 1.25%–2.5% + 1.25%–2.5% (v/v)	–	<ul style="list-style-type: none"> Higher soil nutrients with 10% amendment Optimal dose: 10% Decrease of Ni and TI concentration in pore water 	<ul style="list-style-type: none"> Decrease of pore water pH (minimum 6.7) Increase in Morgans extractable P Decrease of DOC with a dose of 5% Increase in aqueous As, Fe and SO₄ over time 	[115]
Pulp and paper sludge + biosolids (cover; pH = 7.8)	Cd, Pb, Zn (pH = 4.8–8.0)	44 + 66 t/ha	<i>Pascopyrum smithii</i> , <i>Vicia sativa</i> L.	<ul style="list-style-type: none"> Decrease of Zn pore water High concentration of Ca and Mg in plants 	<ul style="list-style-type: none"> P deficiency for plants High Pb value in plants tissue General decrease of Ca, K and Mg concentrations 	[60]
Organic + inorganic						
Biochar (pig manure) + marble mud	Cd, Cu, Pb, Zn (pH = 2.87)	49 g/kg		<ul style="list-style-type: none"> Improvement of soil physical structure (increase of moisture, porosity) High TN concentration 	<ul style="list-style-type: none"> High ash content 	[116]

(Continued)

Table 2. *Continued*

Amendments	Contaminants	Dosage	Vegetation	Advantages	Limits	References
Compost (food waste+ agricultural waste + animal manure + lime; pH = 8.44 ± 0.04) + zeolite	Al, As, Cd, Cr, Cu, Fe, Mn, Pb, Zn (pH = 3.03)	0–50 (w/w)+ 0–12.5 (w/w)	–	<ul style="list-style-type: none"> • Increase of pH • Decrease of Al, Fe, Mn and Zn concentrations • Lower Mn leaching 	<ul style="list-style-type: none"> • Increase of As (1%–158%) and Pb (17%–43%) 	[35]
Compost (green waste; pH = 7.9 ± 0.1) + lime	As, Cd, Cr, Cu, Ni, Pb, Zn (pH = 3.9)	50 + 4.6 t/ha	<i>Agrostis tenuis</i> Sibth	<ul style="list-style-type: none"> • Immobilization of Cu and Zn in soil • Higher biomass accumulation 	<ul style="list-style-type: none"> • Increase of bioavailable As 	[83]
Compost (solid olive mill waste-mature; pH = 8.8) + red mud (pH = 10.9)	As, Pb, Zn (pH = 3.2)	30 + 20 t/ha	<i>Atriplex halimus</i> L., <i>Zygophyllum fabago</i> L.	<ul style="list-style-type: none"> • Increase of soil pH (7.1) • Increase of soil nutrients • Decrease of As, Cd, Cu, Mn and Pb in shoots 	<ul style="list-style-type: none"> • Possible solubilisation of As and Pb [27] • Increase of SO₄ in pore water • Higher Mn, Pb and Zn in <i>Atriplex halimus</i> shoot • Higher Al, As, and Fe in <i>Z. fabago</i> shoot • Increase of aerial accumulation of Mn and Pb 	
Compost (sludge; pH 8.2) + carbocal (pH = 7.2)	As, Fe, Mn, Cu, Ni, Pb, Zn (pH = 2.7)	(2% _{d.w.} [40 t/ha], 5% _{d.w.} [100 t/ha]) + 2%	<i>Cistus ladanifer</i> L., <i>Medicago sativa</i> L.	<ul style="list-style-type: none"> • Best biomass production in plants amended with 100 t/ha compost • Immobilization of metals in plant roots, except Zn • Lower metal accumulation and availability with optimal 0.5% lime • Decrease of Cu, Pb, Mn, Fe and Mg in shoot concentrations (lime + 5% compost) 	<ul style="list-style-type: none"> • Low biomass production in grass [22] with a dosage of 2% • High Mg concentration in plants shoot • High contents of As, Cr, Cu, Ni and Pb in grass • Only <i>M. sativa</i> thrived with addition of 5% compost • High As, Cu and Pb concentrations in shoots of <i>M. sativa</i> 	
Compost (commercial) + eggshells (pH = 7.3)	Cu, Fe, Al (pH = 8.42)	52.5 + 40.5 g/kg	<i>Prosopis tamarugo</i> F. Philippi, <i>Schinus molle</i> L., <i>Atriplex nummularia</i> Lindl.	<ul style="list-style-type: none"> • Decrease of total metal in soil • Decrease of potential transport of Cu, Mn and Pb from root to aerial part of <i>S. molle</i> • No translocation of Mn and Pb from roots to aerial part of <i>A. nummularia</i> and <i>P. tamarugo</i> 	<ul style="list-style-type: none"> • Risk of decrease in bioavailable Fe [99] concentration for plants • Potential accumulation of Pb and Zn in the aerial part of <i>A. nummularia</i> • Potential accumulation of Cd and Zn in the aerial part of <i>P. tamarugo</i> • Potential accumulation of Mn in aerial parts of all plants • Increase in the transport of Fe and Zn to the aerial part of <i>S. molle</i> • Addition of mycorrhizae increase the translocation of Mn and Pb from the roots to the aerial part of <i>S. molle</i> 	

(Continued)

Table 2 Continued)

Amendments	Contaminants	Dosage	Vegetation	Advantages	Limits	References
Manure (pig) + marble waste (pH 7.9–8.6)	Cd, Cu, Pb, Zn (pH = 7.11)	6.25–25 t/ha + 55 t/ha	Herbs, grasses, shrubs (<i>Zygo-phyllum fabago</i> L., <i>Piptatherum miliaceum</i> (L.) Coss., <i>Dittrichia viscosa</i> (L.) Greuter, <i>Phragmites australis</i> (Cav.) Trin. ex Steud, <i>Helichrysum decumbens</i> DC., <i>Sonchus tenerrimus</i> L.	<ul style="list-style-type: none"> • Decrease in soluble Cd and Zn • Improve vegetation cover 	<ul style="list-style-type: none"> • Decrease in soil OM with time 	[32]
Manure (chicken) + lime	Cu (pH = 2.5)	40 + 20 t/ha	<i>Festuca arundinacea</i> Schreb., <i>Bermuda grass</i> (L.) Pers., <i>Paspalum notatum</i> Flüggé, <i>Artemisia capillaris</i> L., <i>Panicum repens</i> L., <i>Sesbania cannabina</i> (Retz.) Poir., <i>Boehmeria nivea</i> (L.) Gaudich., <i>Robinia pseudo-acacia</i> L.	<ul style="list-style-type: none"> • Increase of pH (6.6) and nutrients • Stability of hydrogeochemical and microbiological function of root zone 	<ul style="list-style-type: none"> • Increase of available P 	[57]

In the following, the influences of organic amendments on the physicochemical characteristics of tailings including pH, EC, TOC/DOC, OM, nutrients content and the physical properties will be discussed.

3.1.1. pH and EC

Addition of organic amendments usually increased pore water pH [15,21,27,39]. However, depending on the applied dose, the physicochemical characteristics of the tailings as well as the pH of the organic amendments themselves, pore water pH (particularly of extremely acidic tailings) hardly increased or even decreased [22,40–42]. Such case has been noted with the use of composted sewage sludge (pH 8.2) at low dose (<10% dry weight), where the pH of extremely acidic tailings barely increased (from 2.7 to 3.7–5.1) [22]. Similar effect was also found with the use of compost (from solid olive mill waste, pH 8.8 ± 0.01) and pig slurry (pH 7.8 ± 0.01), at a dose between 60–90 m³/ha [36,43]. Mixed compost (cattle manure + green waste, steer manure), at a dose of 15% (w/w) ± vegetation (grasses), could increase the pH only in a very short term (6 months) before acidification of the tailings occurred [42]. The use of sewage sludge (pH 7.8, at a dose of around 3% dry matter), biosolids (pH 6.85, 6%–12% w/w) and peat (pH 4–7, dose <5%) can even entail pH decrease when used to treat extremely acidic or oxidized tailings [17,40,44–46]. At the opposite, biochars (pH 7.65–11.3, minimum dose of 2%), regardless of the feedstocks and pyrolysis condition, generally increase pore water pH of tailings [30,31,39].

Composts and biosolids are the most common amendments, but they could significantly increase the EC of tailings pore water depending on their quality and raw materials [7,18,20,34,40,47]. However, mature composts (e.g., solid olive mill waste) would not alter pore water EC relative to fresh ones [15,27,48]. Composted organic amendments are suggested to be used rather than raw ones because they have more stable OM, higher CEC and limited spread of pathogens [49–52]. Application of peat (dosage <5%) slightly increased EC whereas biochars (at a dose >2%) significantly increased it, probably due to their important content in ash, depending on the source [8,30,31,46,53,54].

Application of organic amendments in mixture, either between organic amendments or with inorganic materials for an additional alkalinity, is recommended. Biochars would be more efficient when combined with other raw organic amendments, as source of labile organic matter for the development of microorganisms, such as compost or aged manure for the stabilization of extremely acidic and highly contaminated tailings [21,37]. A combination of fresh compost and biosolids are not suggested because they could increase contaminants input. Mixing organic amendments with alkaline materials that could provide additional alkalinity for the stabilization of contaminated tailings was found more effective to increase pH, depending on the dosage (Table 2). The selection of dosage must be completed according to the tailings characteristics (acidic/neutral, highly/slightly contaminated and fresh/oxidized) [34,42]. The dose of alkaline materials could be calculated according to the equivalent amount of CaCO₃ required for the neutralization of acidity by using the method of Sobek et al. [55]. For example, addition of 15.5–55 t/ha limestone/hydrated lime was used to increase the

pH at around 4–5 for tailings having initial pH of 2–3.3, while a dose >200 t/ha would be necessary to increase the pH \approx 6.75 [36,41,43,56]. However, a dose of 20 t/ha of red mud could increase tailings pH from 3.3 to 6.7–7 [27]. Biochars and limestone (pH \sim 7) are frequently used as alkaline materials but biochars are advantageous due to their high pH, contributing to the stabilization and significant increase of tailings pH [21,25,39,41]. When a dose of 20%–80% of biochar was added to compost, acidic soil pH increased from 2.70 to 7.04–8.66, whereas the application of limestone or rockwool (pH 7.1; mixture dose of 30–75 t/ha) + green agriculture wastes (plant remains + strawberry substrate; pH 4.9–7.2) showed very low pH buffering (from 1.6 to 2.1) in a very short period of time (<13 months) [21,41]. Nonetheless, pore water pH of extremely acidic tailings could significantly increase (from 2.5 to 6.6) when lime (20 t/ha) was mixed with manures (chicken, 40 t/ha) [57]. Limestone combined with organic amendments (high OM contents) moderates the buffering of pH, especially when used to reclaim slightly acidic tailings [22].

3.1.2. TOC/DOC and OM

Mature compost is preferred to immature one because the latter could still contain toxic compounds and highly degradable OM, increasing DOC in pore water. In addition, the decomposition of OM in raw or immature organic amendments would be in process until stabilization, decreasing oxygen concentration and, hence, ORP in soil and create a reducing environment [49]. Aged cattle manure increased TOC while composted cattle manure and composted yard manure had no major impact [58]. Slurries (e.g., pig slurry) did not increase pore water TOC/DOC, but even decreased it [36,59]. Biosolids (fresh) and composts (green wastes, sewage sludge, solid olive mill waste) \pm inorganic materials, as well as manures (aged) increased DOC in tailings pore water, denoting their low proportion in humified OM [8,25,27,34,36,58]. Biochars decreased DOC (down to 45%) when produced at more than 600°C [8,39]. Finally, compost (vermicomposted food waste) added with thickened tailings increased OM (14%) [20].

Balancing the mixture of C-rich (e.g., grape residues and olive residues) and N-rich organic amendments (e.g., manure and biosolids) should be performed in order to ensure the optimal C/N ratio, which is an indicator of organic matter's degree of decomposition, for an effective stabilization [34,60,61]. The higher is the C/N ratio, the more stable the OM, and the lower is the DOC. The recommended C/N ratio value to enhance soil fertility and plant development was 20–30; composts have a general value between 25 and 40 [34,62]. The C/N ratio of organic amendments and tailings mixtures controls also N availability for plants from OM mineralization. Low C/N ratios associated to biosolids and manures + inorganic materials can improve soil fertility while olive residues and mature compost can significantly increase the C/N (>30, translated to low N mineralization) and reduce plant aerial biomass [34,49,63,64].

3.1.3. Nutrients

Organic amendments supply nutrients (N, P and K) and organic-C to sterile tailings. Biosolids would provide better nutrients followed by manures, compost, olive processing

solid waste, green wastes, peat and, finally, biochar. Indeed, biochars provided low nutrients [30,37]. Higher OM could be found in peat, followed by biosolids, manure, olive processing olive solid waste and compost. Composts (solid olive mill waste and municipal solid waste), sewage sludge, red mud, olive processing solid waste, paper mill residues increased soluble K (up to 50-fold), and N (up to 94%) [15,36,46,52,65]. Compost from a mixture of municipal green waste + organic waste + pine bark, used alone or mixed with peat, increased extractable P in pore water, which may increase the risk of eutrophication [18]. Other types of compost (mushroom, solid olive mill waste) increased dissolved P, which concentration did not change when combined with inorganic material (red mud derivative) [15,26,27]. Pig manure and sewage sludge provided low organic-C and total N (TN) whereas olive residues and pig slurry increased soil organic-C, dissolved N, K and P [32,34,36]. Composts (rabbit and horse manure, pruning residue, seaweeds and fruit wastes) \pm biochar and pig slurry increased total C and TN [21,36], whereas industrial fertilizer + paper-mill sludge did not increase neither OM nor N and P [66]. Stable organic materials containing recalcitrant organic-C should be combined with other organic amendments source of labile organic compounds in order to promote activation of microbial populations [16].

3.1.4. Physical properties

Composts could increase water holding capacity and CEC, and improve aeration of mine tailings [10,20,67,68]. Biosolids (20%_{dw} anaerobic digested sewage sludge, class B) could increase CEC of tailings while biochars (pruning residues, crop residues and manures) improve water holding capacity [30,37,69]. Mixing inorganic with organic amendments could promote soil structure by increasing aggregates, as indicator of soil fertility, and improves granular structure to facilitate plant establishment [14,69].

In order to select the most performant organic amendments for tailings stabilization, their capacity to mobilize or immobilize metallic elements needs close appraisal.

3.2. Capacity of organic amendments to mobilize/immobilize metallic elements

The performance of organic amendments in mobilizing/immobilizing metallic elements is widely variable depending on their nature and source, as well as tailings characteristics. With respect to redox conditions, the mechanisms of metallic elements immobilization during application of organic amendments and revegetation are sorption, complexation and precipitation [7,22]. Several factors that could impact the mobility/immobility of metallic elements in tailings pore water were identified, such as the pH, ORP, EC, DOC, OM, humification degree, nutrient content (N, P and K), as well as CEC. The pH is the main factor affecting precipitation, while both OM and soil pH affect adsorption sites [7,8,21]. For example, availability of metals such as Mn is influenced by both pH and ORP of soil while Cu is mainly controlled by OM and is less pH-dependent relative to Cd and Zn [36]. Contents in humic acids, OM, DOC and pH affect metals complexation [7]. Generally, single organic amendments were found less effective to treat pore water relative to mixed ones [7,70].

3.2.1. Single application

Organic amendments used alone would be appropriate for tailings stabilization with single metal contamination rather than with multi-elements. Mature organic amendments are also suggested since immature ones could contain high amounts of organic acids, such as fulvic acids which could act as chelating agents for colloidal organic matter, entailing metals liberation in pore water [8,31,36]. In this case, composting of raw organic amendments is suggested; for example, composted cattle manure could be used to immobilize Pb, whereas application of raw cattle manure (aged), which contains fulvic acid, may lead to formation of metal-fulvic acid complexes that would enhance Pb leaching [58]. The use of composts could be also advantageous since they do not necessarily increase metals in soils [52,65]. Compost could be selective in metals mobilization/immobilization depending on its source and tailings characteristics as well as its influence on the physicochemical characteristics of tailings pore water. Composted yard waste was suggested for Zn and Pb immobilization [58]. This amendment would be more efficient to reclaim tailings with a concomitant presence of Fe and Al since the removal mechanism would rather be by sorption onto Fe- or Al-oxyhydroxides. Indeed, the amendment itself could not increase pH above 8 to precipitate Zn or Pb, depending on concentration [58]. Chicken manure compost would promote conversion of acid extractable forms of Cd in soil to residual ones, at a moderate dose (54 t/ha), due to high pH value (8.17), P and OM content [64]. Even though vermicomposted food waste mixed with thickened tailings increased OM (14%), total metal concentrations would not necessarily decrease [20]. Due to its content in hydroxyl, phosphoryl and phenolic functional groups, spent mushroom compost could immobilize Cd, Pb and Cr by sorption [26]. Generally, the use of sewage sludge alone would not be effective to immobilize metals (e.g., Al, Cu, Mn and Pb) in oxidized tailings since the pH of pore water decreased and concentration in soluble metals (e.g., Pb and Zn) increased [17,44]. Biosolids could add contaminants in tailings because they might contain numerous metallic elements (e.g., Al, Fe, Cu, Mn, Zn, Ni, Cr and Pb in sewage sludge), organic contaminants, microplastics, drugs traces and pathogens whereas contaminants encountered in manures only originate from antibiotics, additives and hormones in industrial animal diet (e.g., As to prevent coccidiosis in poultry or Cu to treat weakness of dairy cattle) [7,8,17]. N-rich biosolids (at a dose 6%–12% w/w) would significantly increase Cu and Zn concentrations in pore water but not Mo [34]. Biochars are promising organic amendments because of their capacity to immobilize a wide variation of metallic elements (Cu, Cd, Pb, Ni, Zn and Tl) in tailings due to their high sorption characteristics, except for As [25,30,31,39,71–74]. Their performance to mobilize/immobilize metallic elements depends on their nature (feedstock and pyrolysis parameter) [9,30]. Indeed, biochars made from rice, husk and bran would decrease pore water concentrations of Pb, Cd and Zn, whereas straw char-biochar would increase Pb by up to 26% [75]. Hardwood timber biochar has high porosity, total surface area and CEC; thus, could adsorb Cu and Zn from pore water [76]. Hardwood-derived biochar could mobilize Cu which leaching could be associated to the increase in DOC and tailings pH [77]. Fir tree + manure-biochar, with high pH (10.1), could reduce Cd and Zn concentrations in soil, as opposed

to biochar from fir tree alone with a lower pH (7.65) [30,31]. Pyrolysis temperature could influence also metals immobilization; for example, Cu immobilization in soil could occur when the biochar is produced at high temperature (>600°C) [72]. Biochar combusted at lower temperature (<500°C) and produced with a mixture of manures and residues would be performant due to its high OM (\approx 50%) and carbon contents [30,31,78]. Previous studies also reported that low pyrolysis temperature biochars (\sim 350°C) contain high oxygen, available P, K and Ca, and could immobilize Cu, Ni, Cd and Pb [7,8,72,79].

Species distribution of metals could also change following organic amendments' addition. For example, a small amount of organic amendments (organic-C <2% dry weight in mixture) could be advantageous to create reducing environment, by promoting SO₄ reduction in unoxidized tailings [78]. A mixture of compost and red mud (30 and 20 t/ha, respectively) would decrease the availability of Al³⁺ while Al-hydroxides would become the dominant species [27].

3.2.2. Application in mixture

Better treatment of metallic elements in tailings pore water was found when a mixture between organic amendments (raw/industrial) or with inorganic materials (e.g., limestone and marble waste) was used. The use of biochar (holm oak wood) combined with compost (rabbit and horse manure, pruning residues, seaweeds and fruit wastes) could bind Cu and limit the mobility of Pb and Ni, effect which was attributed to pH increase and the OM provided by the mixture [21]. A combination of biochar and green waste could immobilize Cd and Zn but not Cu and As [8,80]. Using inorganic amendments, particularly limestone, in mixture with organic amendments could be advantageous in so far as during OM mineralization, the liberation of CO₂ enhances CaCO₃ dissolution and metal carbonates formation (e.g., ZnCO₃ and PbCO₃). In addition, CaCO₃ triggers the decrease of EC by precipitation of salts through increase in pH and presence of Ca²⁺ [81]. Furthermore, limestone combined with organic amendments could be used to reclaim slightly acidic tailings, as well as immobilize Mn by precipitation and complexation [22]. In the long term (\approx 20 years), a mixture of compost (preferably mature)/biosolids (high quality, i.e., low metallic elements concentrations) with inorganic materials (lime or gypsum) could immobilize heavy metals (Cu, Cd, Zn and Pb) in tailings with low Fe and Al concentrations [7,15]. Anaerobic and high quality biosolids mixed with inorganic materials could be applied only for low Fe and Al contaminated tailings [10]. However, when compost from green wastes, catering wastes and municipal solid wastes are mixed with lime, total Zn in soil increased [64,82]. Zeolites (pH = 11.78) were also used as they are useful in metallic elements scavenging [8]. The pH increase (from 3 to 7.5–8.1), induced by the addition of zeolite + food waste-based compost, allowed the immobilizing of Al, Fe, Mn and Zn in severely weathered tailings [35]. A mixture of zeolite and biosolids could also immobilize Cd, Cu, Cr, Fe, Mn, Ni, Pb and Zn by transforming the exchangeable and carbonate fractions into residual fractions [8].

Organic amendments are advantageous to immobilize metals in tailings pore water but their influence on metalloids (anions) is uncertain due to their different behavior with negatively charged organic amendments.

3.2.3. Influence on the dynamic of metalloids

Generally, most of organic amendments mobilize metalloids (As, Sb and Se) depending on P, Fe, OM and DOC concentrations, pH and redox condition [7,8,15,27]. The mobilization of As was closely linked to soil pH, which threshold value for higher release started at pH more than 6 [82]. This was mostly observed during the mixing of alkaline materials (e.g., lime and zeolite) with organic amendments [35,83]. It was assumed that the simultaneous presence of CaCO₃ and OM could enhance the mobility of As due to: (1) competition between humic compounds and arsenates in soil, (2) the formation of soluble As-organic complexes, and (3) competition between As and phosphates from the organic amendments [84–87]. When compost from green wastes, catering wastes and municipal solid wastes are mixed with lime, total As in soil pore water increased [82,83]. Amended soil with compost (green waste + municipal solid waste) mixed with lime showed four times increase of As concentration relative to non-amended acidic one [83]. Similarly, amended tailings with compost (food waste + waste + animal manure + lime) mixed with zeolite (dosage 4:1) showed As concentration increase of 1%–158% relative to non-amended ones [35]. However, compost (solid olive mill waste) + hydrated lime could immobilize As, providing that the tailings contain high Fe concentrations (>14%) [27]. Indeed, less As mobilization was noted in tailings containing Fe oxides/hydroxides due to their positive surface charge that could sorb negatively charged As [15,87]. Among the concerns about using compost, as well as pig slurry, is the leaching of As. Nonetheless, compost released lower As than pig slurry due to its low mineralizable organic-C [71]. Organic amendments with high DOC and P should be carefully selected when reclaiming As-contaminated tailings. Biochar was also used as alkaline material substitute but it was found that a high increase in pH could mobilize As(III) in tailings, and can desorb Sb due to electrostatic repulsion [30,88]. Leaching of As was related to OM type. For example, peat humic acid was found to be independent to As leaching. Oppositely, fulvic acid and citric acid can outcompete with As(III) and/or As(V) adsorption at low pH [89].

The next section will discuss the interaction between plants and evolution of soil pore water quality, which are closely related since survival is strongly dependent on the mobilization/immobilization of metallic elements in the pore water.

3.3. Interaction of plants with amended tailings and trace elements

Organic amendments enhance chemical stability of tailings and improve their physical structure. Thus, they facilitate plant establishment [90]. In turn, plants could influence tailings properties and metals availability.

3.3.1. Effects of organic amendments on plants and trace elements

Depending on the type of organic amendments that changes tailings physicochemical properties and metals speciation, shoot metals concentration (frequently Zn) in plants growing on amended tailings might be significant, with

respect to nutrients concentrations, particularly N and P, DOC, organic acid concentrations and plant species [7,8,15,34]. Compost alone could be used to reclaim slightly acidic to neutral and marginally contaminated tailings (at >15% dose) but should be combined with woody plants (e.g., willow species) instead of grasses. However, the stabilization of highly contaminated tailings with 40–100 t/ha of compost + lime would increase shoot concentrations of As, Cu and Pb in herbs (e.g., *Medicago sativa* L.) and Zn in shrubs (e.g., *Cistus ladanifer* L.) [22]. Animal manures (cow, goat, pig and poultry) with low contents of metallic elements, when mixed with inorganic materials, could sustain plant growth and eventually decrease metal concentrations in plant shoots (e.g., Pb and Zn), especially when applied for highly acidic and pyritic mine tailings stabilization [8,32]. Amending tailings with fresh organic amendments are not recommended because the latter could contain considerable fulvic acid which increases metals solubility and bioavailability to plants [32]. Biosolids, grape residues, olive mill residues, goat manure (alone or in mixture) having high DOC that could form organo-metallic complexes (often available, e.g., Cd, Cu and Zn) in water might be unsuccessful for plant growth since the newly formed metal species in soil pore water could be adsorbed by plant roots, subsequently increasing phytotoxicity [34,40]. Manures and cow slurry increased CaCl₂-extractable concentrations of Pb and Zn up to 50 times and their translocation from root to shoot [24].

Depending on the type of biochar, higher metals concentration (Cd, Pb and Zn) could be found in plant shoots (*Anthyllis vulneraria*, subsp. polyphylla (Dc.) Nyman, *Noccaea rotundifolium* (L.) Moench subsp. *cepaefolium*, *Poa alpina* L. subsp. alpina (L.) [30,31]. Nonetheless, biochar reduced the accumulation of metallic elements in shoots, with respect to the type of selected plant (e.g., *Solanum lycopersicum* L.) [80]. Indeed, lower Cd uptake in shoots of *Poa alpina* L. subsp. *alpina* was found relative to *Noccaea rotundifolium* L. after the addition of biochar produced from orchard pruning residues [31]. On the contrary, lettuce and mustard would accumulate Cd in shoots and roots after application of green waste- and chicken manure-derived biochars [91].

Mature and stable organic amendments, with a higher humification degree (thus low DOC) should be used in order to obtain stable chelate, and prevent metals transfer to shoots [34]. For example, olive residues with a revegetation would be beneficial providing it is composted, due to lower content of phytotoxic organic compounds [34]. Olive residues and mature compost can increase significantly the C/N ratio (>30, translated to low N mineralization) and reduce plant aerial biomass [34,49,63,64]. Amended tailings with high P would have synergetic effect which is the great capacity to decrease metal translocation from roots to shoots by the formation of insoluble metal-phosphate in the roots [92]. However, the antagonism effect would be the desorption of As, increasing plant uptake due to site sorption competition with P [8].

Mixing lime with organic amendments would facilitate plants colonization [87]. For example, lime or biochar (e.g., before compost application) would aid to lessen metals availability, accelerate soil development and achieve successful vegetation growth (*Cistus ladanifer* L., *Medicago sativa* L.) [22]. Compost + calcium carbonate improved plant biomass (aerial and roots), for example bushes (e.g., *Atriplex halimus* L.) [15,27].

Dosage of organic amendments with/without inorganic amendments and plant effect could impact redox condition of the tailings and, thus, metals speciation. Better biomass production could be obtained with 5% dry weight of compost (sewage sludge) + lime [22]. Addition of 20 t/ha of red mud alone or in combination with compost (olive mill waste) increased Mn and Tl in shoots, especially Fe and Pb in *Zygophyllum fabago* L. during stabilization of highly contaminated tailings [27]. Recommended dose of chicken manure compost was 54 and 90–200 t/ha for biosolids to limit Cd and Zn (>15 mg/kg) in *Triticum aestivum* L. and *Lolium perenne* L. shoots for the stabilization of slight to moderately contaminated tailings [18,40,64]. Pig manure could promote microbial biomass and activity, and establishment of native vegetation, independently of the dose [32]. A dosage of 1.5% dry weight of biochars (pruning residues, fir tree, manure + fir tree) would be enough to obtain satisfactory aerial mass [30,31]. The application of high doses (>10%; e.g., raw hardwood biochars for the rehabilitation of highly contaminated tailings) could inhibit bioavailable metals/nutrients for plant uptake, especially when combined with grass [25]. An optimal dose of 10%_{dw} would exhibit greater grass growth in the condition to be mixed with other organic amendments at a higher dosage [25].

3.3.2. Plants effects on amended tailings and trace elements

Plant candidates for tailings stabilization should be native, metallophytes (metal tolerant plants not accumulating metals to root tissues), salinity and/or acidity tolerant [10,12,15]. In certain case, for example in semi-arid regions, plants should be adapted to drought [12]. Among the plant species frequently selected for phytostabilization are the type grass, such as *Festuca rubra* L. which has the capacity to translocate low metals concentration from root to shoot [93]. Other types include *Agrostis capillaris* L., *Agrostis castellana* Boiss. & Reuter, *Lolium perenne* L., *Zea mays* L., *Lactuca sativa* L., *Betula pendula* Roth, *Alnus cordata* (Loisel.) Duby, *Crataegus monogyna* Bechst., *Salix caprea* L., *Populus* L., *Larix* Mill., *Brassica* sp., *Pistacia terebinthus* L., *Cistus creticus* L. ssp. *creticus* (L.) Heywood, *Pinus brutia* Ten., *Bosea cypria* Boiss., grasses, vegetable crops and trees [8,94]. Noteworthy, the main objective of phytostabilization is the immobilization of contaminants in plants roots instead of shoots.

Plants absorb soil nutrients in pore water (in particular mineral N and P) from tailings and organic amendments. Moreover, they uptake bioavailable metals from soil pore water, hence limiting metal leaching and reducing indirectly pore water contamination [8,26]. The effect of plants on tailings stabilization include also water absorption by roots, erosion control, increase of macropores in the root zone, and metals binding through root exudates with the aid of OM from the organic amendments [8,10,20,79,90]. A non-desirable plant effects is the possible acidification of the rhizosphere due to mechanisms such as cation exchange balance, root exudation and respiration, release of organic acids, consumption/production of H⁺, that could increase metals concentration (often Zn) in soil pore water [7,21]. Plants can also export trace elements to fauna through browsing which can impact ecosystem functioning. Sunflower can accumulate Cu compared with canola [95]. Grass species should be used only for low contaminated tailings or as a nurse crop [96]. For

example, ryegrass would not be a good candidate for acidic and extremely contaminated tailings [36]. Woody species could be used not only for slight and moderately contaminated tailings but also to reclaim highly contaminated tailings. For example, *Salix alba* L. would be suitable vegetation for Pb stabilization [39]. Coniferous species (jack pine and black spruce) would better survive to reclaim moderately saline tailings than broadleaved trees [20]. *Cassia alata* L. could be interesting since it does not accumulate high concentrations of heavy metals in shoots when used to reclaim multi-metal-contaminated tailings [97]. Plants can also influence C/N ratio of tailings such as the mustard, which increased it [21]. Mustard, type *Brassica juncea* L. could significantly lower soil pH as well due to excess uptake of cations over anions [21].

Other practices to improve plant growth (by promoting rhizobacteria), to enhance plant communities establishment, as well as to decrease metals translocation to plants' shoots were the addition of microorganisms such as fungi (e.g., arbuscular mycorrhizal fungi [AMF]), depending on plants type [98–100]. The inoculation of AMF *Glomus mosseae* increased the biomass of *Coreopsis drummondii* Torr. et Gray (golden wave coreopsis), *Pteris vittata* L. (Chinese brake fern), *Lolium perenne* L. (perennial ryegrass) and decreased Cu in their shoots [101]. AMF such as *Acaulospora* sp., *Rhizophagus irregularis* combined with biochar and/or compost for tailings stabilization decreased Pb, Cu and Zn in shoots of *Jatropha curcas* L. and Cd in *Atriplex nummulari* [98,99,102]. However, compost + AMF increased Pb in *Anthocephalus cadamba* (Roxb.) Bosser [103]. The combination of biochar + compost + AMF would be more effective for plants establishment to reclaim severely contaminated tailings [102]. Some studies even introduced the use of earthworms [104,105]. The combined effect of earthworm (*Pheretima guillelmi*) and AMF (*G. mosseae* and *Glomus intraradices*) increased the growth of *Leucaena leucocephala* Lam. and decreased Pb and Zn concentrations in stems and leaves [106]. However, even though earthworm enhanced soil microbial activity, its use alone would not influence plants metals uptake and could inhibit beneficial effects of AMF [106,107].

3.4. Economic aspects

Cost estimation of tailings stabilization varies depending on the type of mines (coal, gold and polymetallic) due to the differences in the generated contaminants and the subsequent required techniques. Nonetheless, general cost of tailings stabilization ranged between 50\$ and 138\$ million [108,109].

Careful and well-documented approach would be the best option as for tailings management, including prediction tests and modeling methods. However, stabilization costs could be minimized by considering research array that includes (1) environmental impact assessment, (2) early revegetation research program, (3) remote location awareness, (4) materials availability and evaluation of their reuse or recycling.

In summary, organic amendments can change metal speciation (soluble, extractable, residual and insoluble) in soil pore water to make them accessible or unavailable for plants according to the applied doses. Combinations of organic amendments are suggested in order to accommodate the selected type along with the dosage and appropriate plants

Table 3
Suggested amendments and dosage with accompanying plants according to tailings characteristics

Tailings	Amendments	Dosage	Plants
Extremely acidic/highly contaminated	Biochar + compost	20%–80% _{dw} biochar; >10% compost	Trees, shrubs
Extremely acidic/highly contaminated (not with As)	Compost + lime	>15% lime ; >5% _{dw} compost	Trees, woody species
Extremely acidic/highly contaminated	Manure + lime	40–67 t/ha manure; 20–40 t/ha lime	Trees, woody species
Slightly acidic/moderately contaminated	Biochar + compost	5%–10% _{dw} biochar; >5% compost	Trees, shrubs, woody species
Slightly acidic/moderately contaminated (not As)	Manure + lime	6% _{dw} biosolids; >15% lime	Trees, shrubs, woody species
Slightly acidic/moderately contaminated (not As; low Fe and Al)	Biosolids + lime	6%–12% _{dw} biosolids; >15% lime	Trees, shrubs, woody species, grasses
Neutral/moderately contaminated	Biosolids + biochar	6%–12% _{dw} biosolids; 20%–80% biochar	Shrubs, woody species, grasses
	Biochar + green waste	5% _{dw} , -10% _{dw} biochar; -13% _{dw}	Trees, shrubs, woody species, grasses
	Compost (green waste, food waste, cattle manure)	25% _{dw} , -60% _{dw}	Trees, woody species

for tailings stabilization (Table 3). Integrating prediction approaches and the use of available materials in the proximity of the mine area could minimize tailings stabilization costs.

4. Conclusion

This study intends to make a preliminary inventory of organic amendments and their performance in hard rock tailings stabilization and to identify future research avenues for an efficient use. The findings of the study showed that (1) composts, biosolids, biochars are the most frequently used organic amendments during tailings stabilization; (2) generally, organic amendments increased leaching of metalloids (particularly As) in tailings pore water; (3) single organic amendment would be more efficient to reclaim tailings with single or specific contaminant; using mature and composted organic amendments is suggested (e.g., a combination of mature and composted animal manures with inorganic materials might be the most promising option); (4) mixing organic amendments with inorganic materials, along with revegetation was found successful for the stabilization of slightly contaminated tailings; (5) anaerobic and high quality biosolids (low concentration of contaminants) mixed with inorganic materials could be applied only for low Fe and Al contaminated tailings; (6) multi-element contaminated tailings could be remediated with blended industrial (e.g., biochar) and raw organic amendments but phytostabilization is still a challenge; (7) mixtures of compost and biosolids could mobilize mostly metalloids and might increase shoot metal concentrations in plants.

Future research

Research needs to be addressed by future studies that should include the following: (1) the evaluation of the stability of organic amendments, (2) the combined effects of plant and amendment doses on metal speciation and microorganisms communities in rhizosphere, (3) the long-term (>10–20 years) monitoring of reclaimed tailings performance, (4) plants–tailings–microbes interactions should be considered in order to ensure long-term stabilization of metal-contaminated tailings including evaluation of the effects of enzymes that could be released not only by plant roots but also by microorganisms, (5) optimization of organic amendments for the stabilization of hard rock tailings contaminated with As.

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