Innovative amendments derived from industrial and municipal wastes enhance plant growth and soil functions in potentially toxic elements-polluted environments

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Highlights

- *Water treatment residuals, red muds, municipal solid waste compost and biochar can reduce labile PTE in contaminated soils.*
- *When used as amendments, WTR, RM, MSWC and BCH improve soil chemical fertility of PTE-polluted soils.*
- *WTR, RM, MSWC and BCH stimulate soil enzyme activity and heterotrophic bacterial abundance in PTE-polluted soils.*
- *WTR, RM, MSWC and BCH can be used as strategic amendments to enhance plant growth in environments polluted by PTE.*

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Abstract

Potentially toxic elements (PTE), *e.g.* As, Sb, Cd, Cu, Pb, Zn, can severely impact soil element cycling, organic matter turnover and soil inhabiting microbiota. Very often this has dramatic consequences for plant growth and yield which are greatly restricted in PTE-contaminated soils. The use of innovative amendments to reduce the labile pool of such soil contaminants, can result as a feasible and sustainable strategy to improve the fertility and functionality of PTE-contaminated soils as well as to exploit these latter from an agronomic point of view. Water treatment residuals (WTR), red muds (RM), organic-based materials originating from the waste cycle, *e.g.* municipal solid waste compost (MSWC) and biochar (BCH), have emerged in the last decades as promising amendments. In this paper, we report a synthesis of the lessons learned from research carried out in the last 20 years on the use of the above-mentioned innovative amendments for the manipulation of soil fertility and functionality in PTE-contaminated soils. The amendments considered possess physico-chemical properties useful to reduce labile PTE in soil (*e.g.* alkaline pH, porosity, Fe/Al phases, specific functional groups and ionic composition among the others). In addition, they contain organic and inorganic nutrients which can contribute to improve the soil chemical, microbial and biochemical status. This is often reflected by a higher organic matter content in amended soils and/or an increase of the cation exchange capacity, available P and total N and/or dissolved organic C. As a result, soil microbial abundance, in particular heterotrophic fungi and bacteria, and enzyme activities (*e.g.* dehydrogenase, urease and β-glucosidase) are commonly enhanced in amended soils, while plant growth can be significantly stimulated. Overall, the obtained results suggest that the studied amendments can be used to reduce PTE bioavailability in polluted soils, improve soil microbial status and functionality, and enhance the productivity of different crops. This can offer a precious opportunity for the productive recovery of PTE-polluted soils.

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Key words: Water treatment residuals; red muds; municipal solid waste compost; biochar; potentially toxic elements-contaminated soils; plant growth; soil functioning.

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Introduction

Soil pollution by potentially toxic elements (PTE, *e.g.* As, Sb, Cd, Cu, Pb and Zn) represents an increasingly urgent problem at global scale. PTE, unlike organic contaminants, are generally immutable, not degradable and persistent in soil (Adriano *et al.*, 2004). In addition, they can be toxic to plants, animals and soil microorganisms when certain threshold levels are exceeded (Abou Jaoude *et al.*, 2019). Unfortunately, this is not uncommon and is often due to industrial and mining activities, waste incinerators, coal and petroleum combustion, spent ammunition, battery factories, and misuse of pharmaceuticals and pesticides among the others (Silvetti *et al*., 2014). For instance, mining and smelting activities usually produce large amounts of tailings and waste rocks, from which PTE present in primary sulphide ores could spread in soil and other environmentally relevant compartments, *e.g*. surface and groundwater (Wong, 2003; Castaldi *et al*., 2005; Manzano *et al*., 2016), thus posing significant environmental and health risks.

The fertility status of PTE-contaminated soils, intended as the soil capacity to support element cycling and promote plant growth, is commonly affected by the presence of PTE above certain thresholds, which interfere with many metabolic pathways impacting plant and microbial physiology (Castaldi *et al*., 2018; Garau *et al*., 2014, 2017; Visconti *et al*., 2018; Garau *et al*., 2019b). Although such soils cannot be devoted for food or feed production due to their health hazard for humans and animals, they could (and should) be recovered with the aim of limiting the contaminants impact on soil functionality, reduce PTE spread into the environment and promote plant growth. This latter aspect is particularly relevant since the growth of selected plant species in PTE-contaminated soils can be useful for the contaminant stabilization or extraction and such strategies, *i.e*. phytostabilization and phytoextraction, are currently widely investigated worldwide (*e.g*. Kumpiene *et al*., 2014; Garau *et al*., 2014; Castaldi *et al*., 2018). Plant growth in PTE-contaminated environments can reduce soil erosion and spread of contaminants, limit PTE mobility and bioavailability through their immobilization in roots, reduce PTE leaching to groundwater and stimulate microbial activity through the release of root exudates (Castaldi *et al*., 2009b, 2018; Garau *et al*., 2020). Moreover, the cultivation of plant species with phytoremediation capacities, but also able to produce some income, *e.g*. bioenergy crops or other no-food crops, can represent an innovative and sustainable approach for the recovery of PTE-contaminated soils which, however, requires a significant improvement of soil fertility, and above all a reduction of the labile (*i.e*. water-soluble and exchangeable) PTE fractions in soil (Fiorentino *et al*., 2018).

A wide array of techniques has been proposed to remediate PTE-contaminated soils, most of which consist of very expensive or highly invasive treatments that can only be practiced *ex-situ* and have a massive impact on the ecosystem (*e.g*. Mulligan *et al*., 2001). However, alternative low input (and low cost) and more sustainable approaches have been recently proposed for *in-situ* remediation of polluted soils. In particular, in the last decades, a great deal of attention has been put on the evaluation of novel and less impacting strategies for gentle remediation of PTE-contaminated soils (Mench *et al*., 2006; Garau *et al*., 2014; Quintela-Sabarís *et al*., 2017). Such strategies are mainly based on the *in-situ* immobilization of the contaminants using different amendments (or sorbent materials) often deriving from the municipal or industrial waste cycle, *e.g*. compost, Fe-rich by-products, biochar *etc*. (*e.g*. Castaldi *et al*., 2005; Garau *et al*., 2007, 2017; Fellet *et al*., 2014; Yang *et al*., 2016; Zhang *et al*., 2016; Moreno-Barriga *et al*., 2017). Ideally, these amendments should be able to reduce the concentration of labile and bioavailable PTE by sorption and/or (co)precipitation reactions (Basta and McGowen, 2004; Castaldi *et al*., 2005; Manzano *et al*., 2016; Garau *et al*., 2017; Rocco *et al*., 2018), and/or by changing the contaminant speciation (Beesley and Marmiroli, 2011), thereby reducing the chemical stress imposed on plants and soil microorganisms. Importantly, the contribution of such amendments for the recovery of PTE-contaminated soils should not be limited to reduce labile PTE, as this could not be enough to promote plant growth and achieve suitable yields. For instance, adding 3% (w/w) hematite [an iron(III) oxide; Fe_2O_3] significantly reduced labile As in a contaminated mining soil but did not improve *Phaseolus vulgaris* growth which was similar to that achieved in the contaminated untreated soil (Garau *et al*., 2014). This was explained by the authors with bean sensitivity to Fe_2O_3 but could be due also to P deficiency since Fe-oxides have a great affinity for phosphates (Antelo *et al*., 2005; Luengo *et al*., 2006). It is therefore of utmost importance that amendments used for soil remediation are able to improve soil physico-chemical and biological attributes (*e.g*. pH, cation exchange capacity, nutrient supply, microbial abundance, diversity and functionality) other than just reducing labile PTE. The combined presence of such characteristics in each amendment can significantly contribute to plant growth in PTE-contaminated soils and can be the key to achieve economically relevant yields in such environments.

In this review paper, the suitability of several amendments, mainly deriving from the municipal or industrial waste cycle, for the recovery of PTE-contaminated soils and the promotion of plant growth in such environments, will be discussed from a chemical, biochemical, and agronomic viewpoint. In particular, the main physico-chemical features of selected strategic amendments such as municipal solid waste compost (MSWC), red muds (RM), water treatment residuals (WTR) and biochar (BCH) will be presented together with their PTE-adsorption capacities. The amendments impact on the fertility, biochemical and microbial characteristics of different PTE-contaminated soils will be also discussed. Finally, the amendments potential to influence plant growth and PTE uptake in contaminated soils will be also reported with emphasis to selected grass and legume species (*e.g. Lupinus albus, Pisum sativum, Phaseolus vulgaris, Triticum vulgare*) as well as to some multipurpose crops (*e.g. Helichrysum italicum*, *Cynara cardunculus*, *Phragmites australis* and *Arundo donax*).

Origin and physico-chemical features of municipal solid waste compost, red muds, water treatment residuals and biochar

The municipal and industrial waste cycle produces large amounts of by-products which almost always constitute an environmental issue with relevant economic implications. For instance, in 2019, RM deriving from the Alumina industry in Portovesme (Sardinia, Italy) amounted to approx. 20 Mm^3 distributed over 160 ha located in front of the coast line at 26 m asl (Mombelli *et al*., 2019). Drinking water treatment plants also produce continuously large amounts of sludges, *i.e*. WTR, which involves considerable transport and landfill costs. In 2016, WTR production by a typical water treatment plant was estimated of 100,000 t $year^{-1}$ while more than 10,000 t were produced daily on a global scale (Ahmad *et al*., 2016). The same can be said for compost, or more recently for biochar resulting from the transformation of organic (*e.g*. food and green) wastes and whose volumes are constantly increasing due to growing world population. At present, these kinds of materials or by-products mainly represent a problem (and only marginally a resource) while they could be effectively used as amendments for the reclamation of contaminated soils. In particular, MSWC, RM, WTR, and BCH, given their physico-chemical features, could be used as strategic amendments in PTE-contaminated soils, thus improving the fertility of contaminated soils and enhancing plant growth and productivity.

Municipal solid waste compost

Compost is the by-product of a controlled bio-oxidation process carried out by diverse microbial populations under aerobic conditions. The composting process basically involves the degradation of organic residues of plant and animal origin, or green and food waste as in the case of MSWC, and their conversion into a stabilized product. The end product is rich in humus and plant nutrients whereas carbon dioxide, water, and heat are common by-products (Castaldi *et al*., 2009a). The main properties of MSWC are reported in Table 1. Total organic carbon in MSWC is higher than 20% with stabilized organic matter, that is humic and fulvic acids, representing approximately 50% of total organic carbon (TOC; Table 1). The C/N ratio is commonly ~10. Stable compost generally shows high cation exchange capacity (CEC >70 $cmol_{(+)}$ kg^{-1}) and dissolved organic carbon (DOC) content (0.6-1.9 g kg^{-1}). Quantitative assessments of element composition indicate that Fe, Mg and, above all, Ca are abundant in MSWC (Table 1), while the concentrations of Pb, Zn, Cd, and Cu can vary depending on the starting waste and should not exceed the maximum level allowed for organic amendments by the Italian law (Regulation (EU) 2019/1009).

Because of these physico-chemical properties, MSWC could be a strategic resource for the improvement of soil functionality and plant growth in PTE-contaminated soils (Castaldi *et al*., 2005, 2018; Garau *et al*., 2020). Moreover, humic substances of MSWC can immobilize PTE forming complexes of different strengths and reducing their mobility and bioavailability in soil (Paradelo and Barral, 2012; Silvetti *et al*., 2017). This is due to a high surface charge density of humic substances and to their functional groups such as carboxyl, phenolic, hydroxyl, carbonyl, and sulfhydryl which are particularly active in the formation of metal–organic complexes. However, the role of MSWC in the mobility of certain anionic contaminants such as Sb(V) [$Sb(OH)_6^-$] or As(V) [$H_2AsO_4^-$, $HAsO_4^{2-}$] is currently under debate (Udovic and McBride, 2012; Sundman *et al*., 2015; Manzano *et al*., 2016; Diquattro *et al*., 2018) and will be further discussed below.

Red muds

Red muds, a by-product of the Alumina industry, is the alkaline material (pH 10-13) which remains after the digestion of bauxite with caustic soda during alumina extraction in the Bayer process (Garau *et al*., 2007, 2011; Lee *et al*., 2011; Lyu *et al*., 2021). Depending on the quality of bauxite, the amount of RM generated varies between 55 and 65% of the bauxite processed. Roughly 1.0-1.5 Mg of RM are produced for each Mg of alumina and consequently millions of Mg of caustic RM are generated world-wide (*e.g.* about 200 million Mg in 2018; Lyu *et al*., 2021). The main chemical characteristics of RM are reported in Table 1. As mentioned before, RM generally show a low specific surface (<20 m^2 g^{-1}; Castaldi *et al*., 2011) and contain substantial concentrations of Na (*e.g.* > 500 mg kg^{-1} in Garau *et al*., 2011) which can have obvious negative consequences on plant growth, especially for sensitive species. Most of RM are generally made of a mixture of Fe and Al (hydr)oxides such as hematite (Fe_2O_3), boehmite [AlO(OH)] and gibbsite [$Al(OH)_3$], while different tectosilicate-like compounds such as cancrinite [$Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2$] and sodalite [$Na_8Al_6Si_6O_{24}Cl_2$] can be also abundantly present (Castaldi *et al*., 2011; Evans, 2016). As such, RM are not expected to provide soil with mineral elements of plant significance, or to significantly increase soil organic matter, this could imply a limit-

Table 1. Chemical characteristics of municipal solid waste compost, red muds, water treatment residuals and biochar.

Chemical parameters	MSWC	RM	WTR	BCH
pH_{H2O}	7.93-8.86	11.0-11.5	6.45-7.88	8.85-9.30
EC ($mS \cdot cm^{-1}$)	1.24-15.58	2.15-8.70	3.01-5.69	9.91-11.67
Ashes (%)	42.05-46.42	98.45-98.74	42.05-56.67	31.86
Total organic carbon (TOC, %)	24.53-27.34	0.30-0.35	8.42-14.15	41.52-61.32
Dissolved organic Carbon (DOC, g kg^{-1})	0.603-1.944	-	0.101	0.02-2317
Cation Exchange Capacity (cmol(+) kg^{-1})	77.75-93.30	9.8-10.7	75.02	18.81-105.1
Total phosphorus (g kg^{-1})	7.14-13.06	-	0.68-0.89	-
Total nitrogen (N, %)	1.80-2.80	-	0.80-0.87	0.30-1.34
Humic +fulvic acids (HA+FA, %)	12.19-15.34	-	-	-
Total PTE concentration (mg kg^{-1})				
Pb	n.d.-85.00	13.4-48.5	12.17-21.17	n.d.-0.34
Zn	26.91-209	0.025.2	246.03-121.86	n.d.-2.50
Cd	n.d.-0.42	n.d.-1.46	0.24-0.30	n.d.
Cu	n.d.-19.24	0.01-23.9	29.0-51.48	207.1
As	n.d.	n.d.	-	n.d.
Sb	n.d.	n.d.	-	n.d.
Fe	5494-22,929	3035	17,437-245,480	524.8
Mn	140.5-594.73	-	31,636-8645	358.1
Na	993.3-2534	517	32.15-156.46	-
K	1709-2780	-	99.48-3827	-
Mg	4504-5403	-	69.54-2032	-
Ca	63,444-80113	104	89.34-11,027	-

*Data from: Castaldi *et al.*, 2005, 2011, 2014, 2015; Garau *et al.*, 2007, 2011, 2014, 2017; Manzano *et al.*, 2016, 2020; Silvetti *et al.*, 2017; Diquattro *et al.*, 2018; Abou Jaoude *et al.*, 2019, 2020; Garau *et al.*, 2019b. n.d., not detected; MSWC, municipal solid waste compost; RM, red muds; WTR, water treatment residuals; BCH, biochar.

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ed influence on plant growth. However, the high alkalinity of this material can be important to improve element cycling (*e.g*. N-fixation) and soil organic matter turnover in acidic soils, where microbial communities and their functioning are commonly affected by low pH values (Garau *et al*., 2007). Importantly, this also applies to acidic PTE-contaminated soils and can have obvious positive implications for plant growth (Castaldi *et al*., 2009b). Moreover, RM addition to these latter soils can significantly contribute to contaminant fixation due its alkaline pH (PTE in cationic form such as Pb, Cu and Zn tend to precipitate as insoluble oxides or hydroxides as the pH raises) and adsorptive capacity (Fe and Al (hydr)oxides and tectosilicate-like compounds within RM can be very effective at PTE immobilization; Summer *et al*., 1996; Apak *et al*., 1998; Phillips, 1998; Gupta and Sharma, 2002; Santona *et al*., 2006).

Water treatment residuals

WTR are the sludges deriving from the purification of the raw water for civil uses with different coagulants which are added to (co)precipitate particulate organic matter and/or dissolved chemicals from the raw water. The most common coagulants used are aluminium ($Al_2(SO_4)_3 \cdot 18H_2O$), ferric (*e.g*., $FeCl_3 \cdot 6H_2O$) and ferrous (*e.g*., $FeCl_2$, $FeSO_4 \cdot 7H_2O$) salts, which can greatly influence the final WTR composition (Ippolito *et al*., 2011). Although this latter can vary, such amorphous material is characterized by the presence of organic matter (particulate and dissolved) and mineral elements (Castaldi *et al*., 2015; Ippolito *et al*., 2011; Ahmad *et al*., 2016). The chemical properties of WTR (Table 1) makes this sludge a potentially suitable amendment to improve the fertility of degraded soils, such as PTE-contaminated ones, and enhance plant growth therein. Importantly, WTR are characterised by a porous and amorphous nature, mostly made of Al or Fe (oxy)hydroxides [*e.g*. $Al(OH)_3$ or $Fe(OH)_3$] (depending on the coagulant added), which confer to this material a great effectiveness in PTE adsorption (Santona *et al*., 2006; Castaldi *et al*., 2014, 2015, 2018).

Biochar

Biochar, *i.e*. the carbonaceous material originated from the pyrolysis of organic wastes in low-oxygen conditions and variable temperature (200-900°C), is emerging as potentially effective and environmental-friendly amendment for the recovery of PTE-polluted soils (Mehmood *et al*., 2018; Lebrun *et al*., 2019), which also implies the promotion of plant growth in such environments (*e.g*. Ibrahim *et al*., 2017; Yousaf *et al*., 2018). BCH is an alkaline sorbent (Table 1) rich in aromatic carbon that confers a substantial chemical and biological stability to the material, it is also characterized by a porous structure encompassing micro, meso and macro pores (Jindo *et al*., 2014; Xu *et al*., 2017). The pyrolysis conditions (*i.e*. temperature and time) are key factors influencing the physical and chemical properties of biochar, *e.g*. high temperatures (>500°C) decrease biochar acidity and increase its specific surface area (Jindo *et al*., 2014; Xu *et al*., 2017). BCH contains high total organic carbon (generally >40% w/w), extractable P and Ca, while its CEC, total N and DOC are lower than other organic amendments such as compost (Table 1). Like MSWC, PTE concentration in BCH can vary depending on the organic waste of origin and, for its use in agricultural soils, it should not exceed the thresholds imposed by the national norms for amendments and fertilisers (Regulation (EU) 2019/1009).

BCH physico-chemical characteristics (*e.g*. alkalinity, high extractable P and Ca content) make it a suitable amendment for the enhancement of soil fertility (Zhang *et al*., 2013; Li *et al*., 2017), as well as microbial abundance and activity (Gómez *et al*., 2014; Xu *et al*., 2017). Moreover, growing evidence suggest that BCH can have a significant role in decreasing the mobility of PTE (Fang *et al*., 2016; Abou Jaoude *et al*., 2020; Manzano *et al*., 2020). Overall, this is due to its microporous structure and high surface area as well as to the presence of different functional groups (*e.g*. -COOH, Ar-OH, $-NH_2$) able to retain positively and negatively charged PTE species (Xu *et al*., 2013; Bandara *et al*., 2016; Mehmood *et al*., 2018; Qiao *et al*., 2018). In addition, BCH alkalinity can contribute to limit the mobility and bioavailability of selected PTE such as metal cations, through the formation of insoluble Me oxides or hydroxides.

Influence of municipal solid waste compost, red muds, water treatment residuals and biochar on soil physico-chemical characteristics

As discussed earlier, MSWC, RM, WTR and BCH present interesting physico-chemical features which make them promising candidates for improving soil fertility in PTE-contaminated soils. However, the peculiarity of each contaminated soil (*i.e*. specific origin, texture, pH, point of zero charge, organic matter content, relative and absolute PTE abundance and speciation, and so on) requires case by case experimental evidence before proceeding with large-scale interventions. This point should not be overlooked, and the lesson to learn from previous research is that such amendments are not effective in all soils. For instance, adding RM to an acidic soil (pH 4.2) contaminated with Pb, Cd and Zn significantly increased plant growth (Castaldi *et al*., 2009b), while the same RM had opposite results when added to a neutral soil (pH 6.8) contaminated with As, Pb, Cd, and Zn (Garau *et al*., 2014).

Municipal solid waste compost

Compost addition (in the 2-10% w/w range) to PTE-polluted (and unpolluted) soils commonly results in a pH increase between ~1 and 4 units (*e.g*. Castaldi *et al*., 2005; Tandy *et al*., 2009; Huang *et al*., 2016; Manzano *et al*., 2016; Garau *et al*., 2019b; Table 2). For instance, a pH increase from 3.9 up to 7.0 was observed by Alvarenga *et al*. (2008) in a PTE-polluted mining soil after amendment with 100 Mg ha^{-1} MSWC. This can be particularly helpful in (sub)acidic-polluted soils where MSWC addition can reduce the solubility of certain PTE (*e.g*. metal cations) and limit Al toxicity (*e.g*. Castaldi *et al*., 2005; Alvarenga *et al*., 2008; Tandy *et al*., 2009; Manzano *et al*., 2016; Palansooriya *et al*., 2020). In the long term, such pH increase (which is in general proportional to the rate of compost applied; see also Alvarenga *et al*., 2008) is also expected to improve soil organic matter turnover and element cycling which will contribute to providing a better environment for plant growth. Compost addition, especially at a high rate (*e.g*. 4% w/w), can also improve other fertility attributes such as CEC, TOC, available P and total N content (*e.g*. Castaldi *et al*., 2005; Diacono and Montemurro, 2010; Tandy *et al*., 2009; Manzano *et al*., 2016; Garau *et al*., 2019b; Siedt *et al*., 2021; Table 2). For instance, it has been shown that soil organic carbon and humic content can increase up to 30 and 2% respectively after repeated MSWC amendment (Diacono and Montemurro, 2010; Siedt *et al*., 2021). Moreover, remarkable DOC increases were observed in MSWC-amended soils and this was positively correlated with increased microbial abundance and activity (Manzano *et al*., 2016; Abou Jaoude *et al*., 2019; Garau *et al*., 2019b). For instance, DOC

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increased from 42 to 100 and from 74 to 140 mg kg^{-1} soil respectively after 3% (w/w) addition of MSWC to two Lebanese PTE-polluted soils (Abou Jaoude *et al*., 2019). However, the role of DOC in PTE-contaminated soils is rather controversial as, in some instances, it appeared positively correlated with increased PTE solubility (Manzano *et al*., 2016; Palansooriya *et al*., 2020).

Red muds

As anticipated, the addition of RM to polluted soils resulted in significant pH increases, but also higher electrical conductivity (EC) and exchangeable Na (Table 3) (Lombi *et al*., 2004; Garau *et al*., 2007, 2011, 2014; Nejad *et al*., 2021). For instance, adding 2% (w/w) RM to a PTE-polluted mining soil raised the pH from approx. 6.7 up to 8.0 and EC from approx. 100 up to 120 µS cm^{-1} (Nejad *et al*., 2021). Interestingly, a remarkable loss of stabilised soil organic carbon (~40%), and a significant increase of water-soluble C, N, P, phenols and carbohydrates was observed in a PTE-contaminated soil after 2 years since RM addition at 4% (w/w) rate (Garau *et al*., 2011). This was attributed to RM alkalinity and high Na content which likely promoted the dispersion of soil organic matter (SOM) and the consequent release of water-soluble compounds. Unfortunately, the relevance of such phenomenon in terms of plant growth was not reported even if the size and activity of microbial populations in RM-treated soil were significantly increased compared to the untreated polluted soil (Garau *et al*., 2011). This, in turn, could have led to an enhanced/accelerated SOM degradation as a result of co-metabolism and higher enzyme activity (Blagodatskaya and Kuzyakov, 2008; Garau *et al*., 2011, 2014). Finally, Fe and Al (oxy)hydroxides, abundant components of RM (~up to 60%; Castaldi *et al*., 2011), have a great affinity for phosphates ($H_2PO_4^-$ and HPO_4^{2-}) other than toxic arsenates ($H_2AsO_4^-$ and $HAsO_4^{2-}$). Taneez and Hurel (2019) in their review reported arsenate and phosphate removal capacities by RM in the 0.38-68 and 0.58-161 mg g^{-1} range, respectively. This means that P deficiencies can be observed in RM-amended soils as highlighted by Castaldi *et al*. (2009b).

Water treatment residuals

WTR added to polluted soils generally caused moderate increases in soil pH, TOC and CEC, and in some cases also the DOC content increased (Table 2) (Garau *et al*., 2014, 2017; Manzano *et al*., 2016; Zhao *et al*., 2018). For instance, Zhao *et al*. (2016) observed a 63.9% increase of CEC after adding 100 g WTR kg^{-1} soil. An increase of point of zero charge (pH_{PZC}) was reported by Garau *et al*. (2014) in a polluted soil after amendment with 4% (w/w) Fe-rich WTR, *e.g.* from 6.7 to 8.6. This was relevant for the immobilisation of anionic PTE such as arsenates but could be also useful to increase the soil capacity to retain useful anions (*e.g.* phosphates). The increase of soil pH_{PZC} after WTR addition, also reported by Manzano *et al*. (2016) (Table 2), can be explained with the high content of Fe or Al (oxy)hydroxides [*e.g.* ~25% of total Fe was present in the WTR investigated by Garau *et al*. (2014)] which are characterised by pH_{PZC} values between ~7.0-9.0 (Kosmulski, 2016). However, this finding cannot be generalized as decreases of pH_{PZC} were also reported after WTR addition (Table 2).

Table 3. Influence of red muds, added at 4% (w/w) rate, on selected chemical characteristics of an acidic potentially toxic elements -contaminated soil.

	Untreated soil	RM-soil
pH_{H2O}	6.84	8.80
Electric conductivity (µS cm^{-1})	214.5	351.5
Total organic C (g kg^{-1})	39.34	33.03
Water soluble C (g kg^{-1}d.m.)	3.40	7.08
Total N (g kg^{-1})	1.53	1.22
Point of zero charge (PZC)	6.68	4.71
Total PTE concentration (mg·kg^{-1})		
As	2105.28	2020.38
Cd	18.04	17.38
Cu	264.78	243.86
Pb	714.05	685.46
Zn	522.53	518.93

Data from Garau *et al.* (2014). RM, red muds; PTE, potentially toxic elements.

Table 2. Influence of municipal solid waste compost and water treatment residuals, added at 4 and 2% (w/w) rate respectively, on selected chemical characteristics of different potentially toxic elements-contaminated soils (S1, S2 and S3).

	S1			S2			S3		
	Untreated	MSWC	WTR	Untreated	MSWC	WTR	Untreated	MSWC	WTR
pH_{H2O}	3.77	7.87	4.47	7.58	7.82	7.46	8.10	8.22	7.94
pH_{PZC}	4.60	4.90	4.00	7.90	8.10	8.10	6.60	6.60	7.10
EC (dS·m^{-1})	0.44	0.45	0.68	0.33	0.55	0.32	0.26	0.40	0.33
CEC(cmol(+) kg1)	10.07	11.44	12.15	12.34	17.44	16.52	21.47	24.67	16.52
TOC (%)	1.04	1.93	1.51	2.50	2.95	2.66	4.15	4.90	4.54
DOC (mg kg^{-1})	30.12	240.3	36.23	190.3	340.6	157.2	432.4	438.4	432.6
Total N (%)	0.03	0.07	0.08	0.16	0.18	0.14	0.08	0.09	0.13
Total PTE concentration (mg·kg^{-1})									
As	22,661			371			749		
Pb	2162			124			74		
Cu	412			46			19		
Zn	1535			279			57		

Data from Manzano *et al.* (2016). MSWC, municipal solid waste compost; WTR, water treatment residuals; PTE, potentially toxic elements.

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Biochar

Similarly to the other amendments, BCH addition to PTE-polluted soils generally resulted in a pH increase which was due to its alkaline nature (*i.e*. BCH pH is mostly in the 8.9-9.3 range; Table 1). Importantly, also CEC and OM content generally increased after BCH amendment (Table 4) (Abou Jaoude *et al*., 2019; Lebrun *et al*., 2019; Manzano *et al*., 2020). Depending on the biochar type, DOC content significantly increased in treated soils (Abou Jaoude *et al*., 2020), while it decreased in others (Table 4; Manzano *et al*., 2020). This can be explained with the different DOC content of the BCH added, which in turn depends on the organic biomass and pyrolysis conditions, as well as by a certain adsorption capacity of BCH. For instance, the BCH used by Abou Jaoude *et al*. (2020) was obtained at low temperature (*i.e*. 400°C) by MSW, and had a DOC content of 2300 mg kg^{-1}, while that of Manzano *et al*. (2020) was obtained at high temperature (*i.e*. 800°C) by softwood and contained approx. 0.02 mg kg^{-1} DOC. Such a low DOC content suggested that almost all biochar's C was recalcitrant and insoluble. Importantly, when this latter BCH was added to two different PTE-polluted soils, the DOC content significantly decreased indicating that BCH actively adsorbed dissolved organic compounds in soil (Table 4; Manzano *et al*., 2020), as also reported by other authors (*e.g*. Lin *et al*., 2012; Eykelbosh *et al*., 2015). As anticipated, this can have relevant consequences on the size and activity of soil microbial populations and indirectly on plant-growth. Different researchers reported high amounts of available P and exchangeable Ca in BCH that are supplied to the amended soils, mostly resulting in significant increases (*e.g*. Glaser and Lehr, 2019; Jien and Wang, 2013). For instance, Glaser and Lehr (2019) reported that BCH increased P availability in agricultural soil by a factor of 4.6 irrespective of the feedstock used. Our experimental evidence supports such conclusions, *e.g*. available P significantly increased from 31 to 40 and from 37 to 56 mg kg^{-1} in two PTE-contaminated soils treated with 5% (w/w) softwood BCH (Table 4; Manzano *et al*., 2020). Significant increases in exchangeable Ca were also reported in the same study.

Generally, the addition of MSWC, RM, WTR and BCH did not cause a significant change in the total concentration of soil PTE (Castaldi *et al*., 2005; Garau *et al*., 2007, 2011, 2014, 2017; Manzano *et al*., 2016, 2020; Abou Jaoude *et al*., 2019, 2020; Garau *et al*., 2019b). This is a fundamental prerequisite for the use of these amendments in contaminated (but also uncontaminated) soils and should be always verified before proceeding with any other investigation.

Influence of municipal solid waste compost, red muds, water treatment residuals and biochar on labile potentially toxic elements in contaminated soils

The aim of *in-situ* immobilization of PTE is to reduce their labile fractions, *i.e*. water-soluble and potentially bioavailable ones (*e.g*. easily exchangeable PTE), which impact most soil (micro)biota (including plants) and soil biochemical functioning.

Table 4. Influence of a softwood-derived biochar on physico-chemical characteristics of the different potentially toxic elements-polluted soils.

Chemical analyses	Soil 1		Soil 2	
	Untreated	BCH-soil	Untreated	BCH-soil
pH_{H2O}	6.82	7.23	7.95	7.92
EC (µS cm^{-1})	377	345	454	404
Ash (%)	91.90	92.40	91.70	90.90
CEC (cmol(+) kg^{-1})	22.80	22.60	18.60	20.70
Total organic matter (OM, %)	4.71	11.85	4.05	15.04
Total C (%)	2.79	6.93	2.36	8.74
Total N (%)	0.22	0.23	0.11	0.12
Total carbonate (%)	n.d.	n.d.	3.60	3.90
DOC (mg g^{-1})	0.80	0.67	0.35	0.19
Available P (mg·kg^{-1})	31.00	40.10	37.21	56.17
Exchangeable K (cmol(+) kg^{-1})	1.19	0.99	1.11	1.03
Exchangeable Ca (cmol(+) kg^{-1})	10.66	12.49	20.02	20.53
Exchangeable Mg (cmol(+) kg^{-1})	2.54	2.54	2.08	2.26
USDA texture	Sandy Loam		Sandy Loam	
Total PTE concentration (mg·kg^{-1})				
Total Sb	1.31		18.88	
Total As	31.83		39.34	
Total Cd	4.75		74.03	
Total Fe	3274		3670	
Total Mn	626.7		1245	
Total Pb	317.67		1899	
Total Cu	41.13		136.5	
Total Zn	622.2		3803	

Data from Manzano *et al.* (2020). BCH, biochar; PTE, potentially toxic elements.

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Effective amendments are able to immobilize PTE through different mechanisms encompassing surface adsorption (by inner and outer sphere complexation), structural incorporation and/or precipitation (Castaldi *et al*., 2011, 2015; Silvetti *et al*., 2017). As mentioned before, this is an essential prerequisite to facilitate and stimulate plant growth in PTE contaminated soils. Common soil PTE include oxyanion (*e.g*. arsenates, antimonate) and cationic species (*e.g*. lead, copper, cadmium, zinc) which show a different affinity (*i.e*. binding capacity) for the functional groups present on the amendment surfaces. This makes very challenging the selection of effective amendments for the immobilization of anionic and cationic PTE co-occurring in soil.

Influence of amendments on labile potentially toxic elements in oxyanionic form

Single step and/or sequential extraction procedures can be used to assess the amendments influence on labile and potentially bioavailable As and Sb oxyanions [*i.e*. $H_2AsO_4^-$, $HAsO_4^{2-}$ and $SbOH_6^-$] (*e.g*.; Wenzel *et al*., 2001, Van Vleek *et al*., 2011; Tan *et al*., 2018). For instance, the sequential extraction procedure of Wenzel *et al*. (2001) requires that soil samples are treated with $(NH_4)_2SO_4$ solutions to extract the non-specifically sorbed anionic PTE (Fraction 1). Then, the same soil samples are treated with $NH_4H_2PO_4$ solutions to extract the specifically sorbed As and Sb (Fraction 2); subsequently they are treated with NH_4^+-oxalate buffer solutions to extract the PTE associated with amorphous and poorly crystalline Fe and Al hydrous oxides (Fraction 3). Finally, soil samples are treated with NH_4^+-oxalate buffer and ascorbic acid solution to extract As and Sb associated with well-crystallized Fe and Al hydrous oxides (Fraction 4). After the last step of the sequential extractions, residual PTE in soil are determined after acid digestion with H_2O_2 and HNO_3 + HCl (3:1 ratio).

Single step and/or sequential extraction procedures, despite accepted limitations (Nirel and Morel, 1990), can provide useful evidence on PTE distribution in soil (*i.e*. quantify mobile and less mobile fractions) after amendment addition.

Municipal solid waste compost

Several studies showed an increase of labile As in polluted soils treated with MSWC (*e.g*. Manzano *et al*., 2016). For example, exchangeable and water-soluble As increased (>65% compared to untreated soil) in an ex-mining soil treated with 4% w/w MSWC (Manzano *et al*., 2016). This was explained with: i) the competition between low molecular weight dissolved organic anions within MSWC and As for the same retention sites in soil (Tandy *et al*., 2009); ii) the potential of specific inorganic anions in compost (*e.g*. phosphates) to displace As from Fe-oxide phases (Fitz and Wenzel, 2002); iii) the formation of As-(Me)-DOC soluble complexes (note that the soil was co-contaminated by As and metals such as Pb, Cd, and Zn; Manzano *et al*., 2016). However, other studies showed that compost had no obvious effect on water-soluble and easily exchangeable As and Sb, and no mobilization was observed (Garau *et al*., 2017; Garau *et al*., 2019b). In particular, Garau *et al*. (2019b) showed that water-soluble and exchangeable As in a multi PTE polluted soil did not significantly differ in MSWC-treated and untreated soils; while Sb significantly decreased in treated soil with respect to control (*e.g*. <19%). Likewise, a significant decrease of labile Sb and As was also recorded by Abou Jaoude *et al*. (2020) after MSWC addition (3% w/w) to different PTE-contaminated soils.

Red muds

RM addition to a PTE-polluted soil gave a significant decrease of water-soluble As even if the exchangeable As increased (Figure 1; Garau *et al*., 2011). RM is mainly a complex mixture of Fe/Al (hydr)oxides such as hematite, gibbsite, boehmite and others (Castaldi *et al*., 2011) which show a great affinity for arsenates. These can be immobilized on RM surfaces by weak (*e.g*. electrostatic) or more stable (bidentate or binuclear) interactions (Castaldi *et al*., 2011). Such RM effect on water-soluble As was not observed in other studies (*e.g*. Garau *et al*., 2014) where, however, water-soluble and exchangeable As were extracted in a single step and could not be discriminated. Therefore, this does not rule out the possibility of a reduction of water-soluble As triggered by RM.

Concerning the immobilization of soil Sb by RM, very few reports can be found in literature. Tandy *et al*. (2017) showed that high amounts (*i.e*. 12.5:50 RM to soil ratio, w/w) of RM-based amendments (*i.e*. ViroSoil™) were effective at reducing Sb leaching in moderately contaminated shooting range soils. Similar findings were reported by Sanderson *et al*. (2015) which showed a reduction of water-extractable Sb (greater than 50% in the four shooting range soils analysed) after the addition of neutralized (with gypsum) RM at 0.5% (w/w).

Water treatments residuals

Labile As generally decreased in soils amended with Fe-rich WTR, likely as a consequence of stable complexation of As by Fe (hydr)oxides (Fendorf *et al*., 2010; Castaldi *et al*., 2014; Garau *et al*., 2014; Nagar *et al*., 2015; Manzano *et al*., 2016). For instance, an approximate 27% reduction (*vs* control) of labile As was observed in a WTR-treated soil by Garau *et al*. (2014). By contrast, no obvious effect of WTR on labile Sb was observed in other studies (*e.g*. Garau *et al*., 2017). However, it should be noted that in this latter case, total Sb in soil was low (~100 mg kg^{-1}) and WTR was mixed with MSWC in a 1:1 ratio (w/w), which could have masked the actual WTR effect.

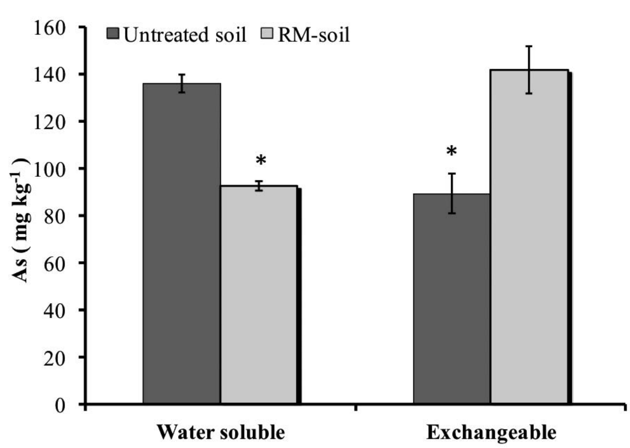

Figure 1. Water soluble and exchangeable As fractions extracted from an untreated and a red muds (RM)-treated potentially toxic elements-polluted soil. Red mud was added at 4% (w/w) rate. Mean values±standard deviations (error bars) are reported. For each fraction asterisks denote statistically significant differences (Student's t-test; P<0.05). Data from Garau *et al.* (2011).

Biochar

A decrease of labile As and Sb in BCH-treated soils has been detected by Abou Jaoude *et al*. (2020). In particular, these authors reported a significant decrease of water soluble and exchangeable As and Sb (up to ~48 and 33% respectively) in PTE-polluted soils treated with 3% (w/w) BCH, with respect to unamended soils. Such decreases suggested a strong binding affinity of both PTE with BCH. This might be due to the presence of amorphous Fe or Al (hydr)oxides within the biochar and to their well-known affinity towards anionic species in soil (Castaldi *et al*., 2014; Fang *et al*., 2016; Qiao *et al*., 2018; Abou Jaoude *et al*., 2020).

Influence of amendments on labile potentially toxic elements in cationic form

Likewise As and Sb, the mobility and potential bioavailability in soil of metal contaminants (*e.g*. Pb, Cd, Cu, Cr, Ni and Zn) can be assessed using single step or sequential extraction procedures. Note that the very different characteristics of metal cations and oxyanion contaminants in soil require diverse extractants and sequential extraction procedures, *e.g*. Wenzel *et al*. (2001) for anionic PTE such as As and Sb, Tessier *et al*. (1979), Basta and Gradwhol (2000), Rao *et al*. (2008) for metal cations such as Pb, Cu, Zn, Cd and Ni. Regarding the sequential extraction of cationic PTE proposed by Basta and Gradwhol (2000), soil samples are first treated with $Ca(NO_3)_2$ solution to extract metal (Me)-exchangeable pool (Fraction 1); afterwards, the same soil samples are treated with NaOAc solutions to extract Me forming weak surface complexes (Fraction 2); finally, soil samples are treated with Na_2EDTA solutions to extract surface complexed and precipitated Me (Fraction 3). After the last step of the sequential extractions, residual PTE in soil are determined after acid digestion with H_2O_2 and HNO_3 + HCl (3:1 ratio).

Municipal solid waste compost

Compost addition (especially when added at high rate, *e.g*. 4 or 10% w/w) decreased significantly water-soluble and readily exchangeable PTE in soil, *e.g*. Pb, Cu, Zn, Cd, and Ni (Castaldi *et al*., 2005; Manzano *et al*., 2016; Garau *et al*., 2017; Abou Jaoude *et al*., 2019; Garau *et al*., 2019b); as for As and Sb, this is relevant since these fractions represent the most labile and potentially bioavailable PTE pool (Manzano *et al*., 2016). Garau *et al*. (2019b) observed that MSWC decreased labile Cd by 32% and 47% when 2% and 4% (w/w) compost respectively was added to a strongly polluted mining soil (Figure 2). Such decreases, as well as those observed for other metal cations, could be ascribed to the capacity of MSWC to retain PTE through specific adsorption mechanisms (Park *et al*., 2011; Garau *et al*., 2014), as well as to the involvement of compost water-soluble fraction in the formation of poorly soluble PTE-precipitates (Castaldi *et al*., 2005, 2015, 2017; Park *et al*., 2011; Garau *et al*., 2014, 2017; Silvetti *et al*., 2017; Manzano *et al*., 2016). In this sense, it was recently shown that phosphate, chloride and sulphate anions within MSWC were able to precipitate Pb and Cu ions present in solution (Castaldi *et al*., 2017). Also, the pH increase which occurred in compost-amended soils likely favoured: i) the deprotonation of specific functional groups of OM (*e.g*. carboxyl groups) eventually leading to an increase of stable (*i.e*. inner sphere) PTE complexes (Wang and Mulligan, 2009); ii) the formation of PTE precipitates in the form of metal oxides or hydroxides. Nevertheless, some studies reported an increase of water soluble and exchangeable Zn and Cd (*e.g*. Beesley and Dickinson, 2010; Manzano *et al*., 2016; Abou Jaoude *et al*., 2019) after MSWC addition to soil. This phenomenon, which was also observed for As, was explained with the formation of soluble complexes between Zn or Cd and DOC compounds (Martínez *et al*., 2003). Besides, it cannot be excluded that divalent metal cations abundant in MSWC (such as Ca and Mg), and readily released in the soil solution, could have affected the mobility of Zn by means of ion exchange (Branzini and Zubillaga, 2012; Manzano *et al*., 2016).

Red muds

Garau *et al*. (2014) detected a significant increase of water-soluble Zn, Cu and Cd in a contaminated soil amended with RM (Figure 3). This was explained by the increased concentration of water-soluble metal-organic complexes deriving from the alkaline dispersion of native soil organic matter induced by RM (Garau *et al*., 2011, 2014). However, Garau *et al*. (2007) observed a high reduction of water-soluble and exchangeable Cd, Pb and Zn in an acidic contaminated soil (pH 4.2) treated with 4% (w/w) RM. For instance, water-soluble Zn decreased from 87 to 8.7 mg kg^{-1} soil, while exchangeable Zn reduced from 244 to 15 mg kg^{-1}. This was explained with the increase in pH (from 4.2 to 7.1) in this RM-treated soil, which favoured the precipitation of Me oxides or hydroxides, as well as with metal adsorption by variably charged colloids such as Fe and Al (hydr)oxides within RM (Taneez and Hurel, 2019).

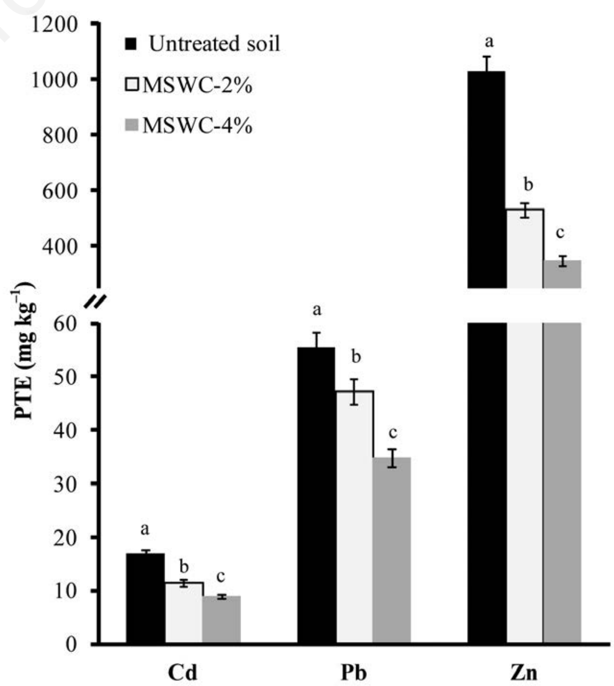

Figure 2. Water soluble Cd, Zn and Pb fractions extracted from an untreated potentially toxic elements (PTE)-polluted soil and from the same soil treated with 2 and 4% (w/w) municipal solid waste compost (MSWC). Mean values±standard deviations (error bars) are reported. For each PTE, different letter on top of each bar denote statistically significant differences (Fisher's least significant different test; P<0.05). Data from Garau *et al.* (2019b).

Water treatment residuals

The impact of WTR on labile Me in soil was variable. In particular, WTR reduced or did not change significantly water-soluble and exchangeable PTE such as Pb, Zn and Cu (Garau *et al*., 2014; Manzano *et al*., 2016). The reduction was mainly explained with the capacity of the organic and inorganic components of WTR to chemically adsorb PTE (*i.e*. Park *et al*., 2011; Garau *et al*., 2014). Importantly, we are not aware of labile PTE increases after WTR addition.

Biochar

Biochar was able to significantly reduce water-soluble and readily exchangeable PTE in polluted soils (Abou Jaoude *et al*., 2020; Manzano *et al*., 2020). Manzano *et al*. (2020) showed that labile Cd, Zn and Pb were reduced by 29%, 55% and 79% in a multi PTE polluted soil treated with 5% (w/w) BCH. This was explained by different factors such as: i) the liming effect of BCH (Houben and Sonnet, 2015); ii) the PTEs complexing capacities of BCH by means of its carboxylic and phenolic functional groups (Abou Jaoude *et al*., 2020; Qiao *et al*., 2018); iii) the influence of BCH inorganic components (CO_3^{2-}, OH^-, PO_4^{3-}) in the formation of PTE precipitates, *e.g*. lead carbonates [$PbCO_3$ and $Pb_3(CO_3)_2(OH)_2$] and lead phosphates [$Pb_5(PO_4)_3(OH, Cl)$ and $Pb_9(PO_4)_6$] (*i.e*. Cao *et al*., 2003; Beesley *et al*., 2014; Bandara *et al*., 2016; Manzano *et al*., 2020; Abou Jaoude *et al*., 2020).

Influence of municipal solid waste compost, red muds, water treatment residuals and biochar on the heterotrophic microbial community and biochemical functioning in potentially toxic elements-contaminated soils

Most often, the selection of an amendment for the *in-situ* treatment of contaminated soils is primarily based on its chemical performance, *i.e*. the ability to reduce the concentration of labile PTE. By contrast, additional effects such as the amendment impact on soil microbial abundance, diversity and functionality are often neglected as well as the impact of the amendment on the soil microbial community. However, it is widely recognized that the soil microbial component can affect many key ecosystem processes, *e.g*. the biogeochemical cycle of plant nutrients, as well as stimulate plant growth (Garau *et al*., 2005). Therefore, the maintenance and/or improvement of soil microbial abundance, diversity and functionality following amendment addition should be of primary importance to support ecosystem services and possibly allow for increased plant yield (Garau *et al*., 2014, 2017, 2019a).

Readily culturable heterotrophic bacteria and fungi are a small component of the total soil microbial community (1-5%; van Elsas *et al*., 2006), yet their relevance in terms of both biomass and activity can be much greater. As pointed out by Ellis *et al*. (2003), a positive correlation has been shown between activity and cell size, cell size and culturability, and activity and culturability. Moreover, given the very small size of the numerically dominant unculturable microbial cells in soil, these latter are not expected to contribute greatly to soil microbial biomass or metabolic activity (Ellis *et al*., 2003). For these reasons, the number of readily culturable microorganisms can be used to estimate the potentially active microbial populations in soil, *i.e*. those involved in soil organic matter turnover and in the cycling of elements essential for plant growth, *e.g*. N and P (*e.g*. Timms-Wilson *et al*., 2006; Mohapatra, 2008; Ventorino *et al*., 2018; Garau *et al*., 2019a).

Soil enzymes (mostly, even if not exclusively, released by microbial cells) play a central role in such processes mediating and regulating the organic matter decomposition and contributing to soil fertility (Oliveira and Pampulha, 2006; Bhattacharyya *et al*., 2008). Given their sensitivity to PTE, soil enzyme activities are often reduced in contaminated soils and this is expected to negatively affect soil fertility and plant growth (Bhattacharyya *et al*., 2008; Oliveira and Pampulha, 2006; Garau *et al*., 2019a). Identifying suitable amendments, able to increase heterotrophic microbial populations and stimulate biochemical functioning in PTE-contaminated soils, can be therefore relevant for improving soil fertility and establishing higher crop yields in contaminated environments.

Municipal solid waste compost

The addition of MSWC or mixed amendments containing compost, to PTE-contaminated soils generally increased the number of culturable heterotrophic bacteria (Garau *et al*., 2017, 2019a). Bacterial number (expressed as Log_{10} CFU g^{-1} soil) increased from 5.81 to 6.61 after the amendment of a mining technosol contaminated by Sb, Pb, Cd and Zn with 1% MSWC + 1% WTR (Garau *et al*., 2017). The same effect was observed on culturable fungi (from 4.79 to 5.00 Log_{10} CFU g^{-1} soil) and actinomycetes (from 5.57 to 6.19 Log_{10} CFU g^{-1} soil). Similar trends were observed in different soils heavily contaminated with As (up to 22,661 mg kg^{-1}) and variable amounts of co-occurring metals, *i.e*. Pb, Zn, and Cu (Garau *et al*., 2019a). In this case, MSWC was the most effective amendment at increasing the population size of total culturable

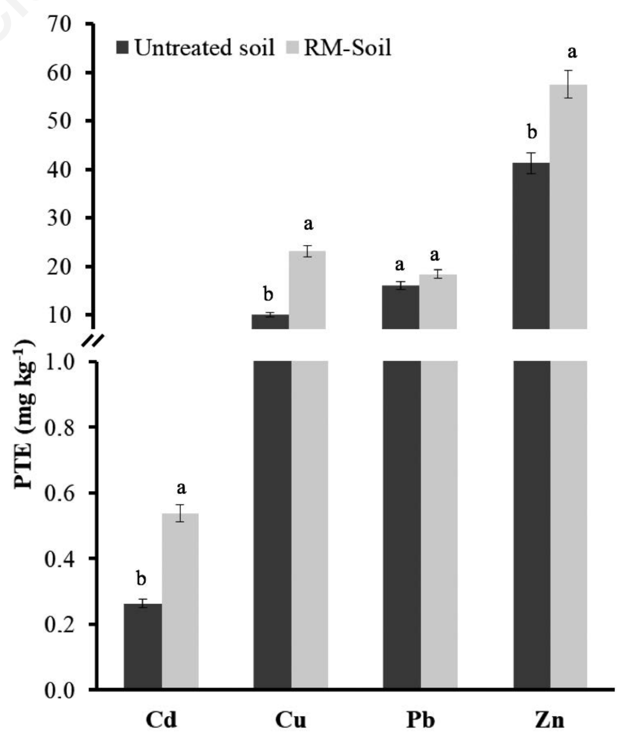

Figure 3. Water soluble Cd, Cu, Pb and Zn extracted from an untreated potentially toxic elements (PTE)-polluted soil and from the same soil treated with red muds (RM) at 3% rate. Mean values±standard deviations (error bars) are reported. For each PTE, different letter on top of each bar denote statistically significant differences (Fisher's least significant different test; P<0.05). Data from Garau *et al.* (2014).

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bacteria (soil treatments with WTR and MSWC+WTR were also included in the study; Figure 4), while the number of fungi generally decreased (up to <14%; Garau *et al*., 2019a). Overall, this was explained by a reduction of labile PTE in soil, due to compost fixing abilities, and to the release of C compounds from MSWC which sustained microbial growth in amended soils.

These results were supported by an improved biochemical functioning in amended soils. In particular, dehydrogenase activity (DHG), which reflects the capacity of several intracellular enzymes to oxidize organic molecules, was increased up to ~20 fold after 4% (w/w) MSWC addition (Garau *et al*., 2019a, 2019b; Figure 5). However, both inhibitory and stimulating effects were observed for urease activity (URE) that catalyses a specific step of the N cycle, *i.e.* urea conversion to NH_4^+ and CO_2 (Speir *et al*., 1999; Bhattacharyya *et al*., 2008; Sigurdarson *et al*., 2018). For instance, Garau *et al*. (2019b) observed that URE decreased by 32% and 60% in polluted soils amended with 2% and 4% (w/w) MSWC. This appeared in contrast with the lower potential bioavailability of PTE observed in the amended soils but could be explained by the formation of humus-enzyme complexes with reduced catalytic activities (Pascual *et al*., 2002). Moreover, the inorganic N released by MSWC could have inhibited urease synthesis by soil microbial populations contributing to explain the reduced URE activity detected in amended soils (Castaldi *et al*., 2009a; Garau *et al*., 2019b). Nonetheless, increased URE activity values were observed in contaminated soils treated with MSWC (Abou Jaoude *et al*., 2019; Garau *et al*., 2019a). In particular, Garau *et al*. (2019a) showed that URE activity in compost treated soils increased up to ~7.4-fold, suggesting that PTE contamination can have negative influences on soil N cycle and that MSWC addition can be helpful to alleviate and/or reverse such negative impact (Bhattacharyya *et al*., 2008; Abou Jaoude *et al*., 2019).

The β-glucosidases activity (GLU), due to extracellular enzymes involved in soil C cycle (*i.e.* they cleave β 1 → 4 bonds linking two glucose or glucose substituted molecules; Alvarenga *et al*., 2008; Bastida *et al*., 2012), was significantly enhanced in polluted soils treated with MSWC (Abou Jaoude *et al*., 2019; Garau *et al*. 2019a, 2019b). Abou Jaoude *et al*. (2019) highlighted MSWC as the most effective amendment at favouring GLU, *i.e.* it stimulated a 117-fold increase of GLU with respect to control soil. This was likely due to the increase of labile C in amended soils (Alvarenga *et al*., 2008; Novak *et al*., 2018) and to a decrease of labile PTE (Bhattacharyya *et al*., 2008; Garau *et al*., 2019b). As for URE, other reports indicated that GLU activity decreased in MSWC-treated soils (Miller *et al*., 1998; Garau *et al*., 2014, 2017, 2019a). Considering that fungi are the predominant source of β-glucosidases in soil, the reduced GLU activity could be due to an altered fungal/bacterial ratio, where bacteria prevailed in MSWC-treated soils (Garau *et al*., 2019a).

Red muds

Red mud addition caused a significant increase of soil microbial biomass-C and fast-growing heterotrophic bacteria in PTE-contaminated soils (*e.g.* Garau *et al*., 2007, 2014). This latter microbial population increased up to 10-fold in an RM-treated soil (4% w/w) with respect to the control (*e.g.* Garau *et al*., 2007, 2011, 2014). Such increases were not simply due to a reduction of labile PTE and/or to an improvement of other soil chemical parameters which could promote microbial growth (*e.g.* soil pH), but also to the ability of RM to disperse the stable soil organic matter and increase the DOC in soil pore water (Lombi *et al*., 2004; Garau *et al*., 2011, 2014). As opposed to culturable bacteria, the number of heterotrophic fungi decreased significantly or did not show any substantial variation in size after the addition of RM (Garau *et al*., 2007, 2014). As previously mentioned, this was apparently due to the RM influence on soil pH which favoured the growth of bacteria at the expenses of fungi (Strickland and Rousk, 2010; Garau *et al*., 2014).

Increased DHG activity (~43-60%) was observed by Garau *et al*. (2007, 2011, 2014) in RM-treated soils and this was the result of a higher bacterial abundance probably due to the higher PTE-immobilization in amended soils. In this regard, a highly significant correlation was found between DHG and culturable heterotrophic bacteria (r=0.86, P<0.0001) in different PTE-contami-

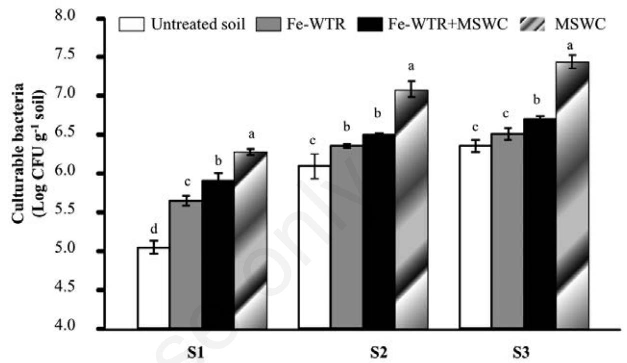

Figure 4. Total culturable heterotrophic bacteria in different untreated potentially toxic elements (PTE)-contaminated soils (S1, S2 and S3) [untreated] and in the same soils treated with water treatment residuals (WTR) at 2% (w/w), WTR at 1% (w/w) + municipal solid waste compost (MSWC) at 2% (w/w) and MSWC at 4% (w/w). For each soil, different letter on top of each bar denote statistically significant differences (Tukey-Kramer multiple comparison test; P<0.05). Data from Garau *et al.* (2019a). Total PTE content in S1, S2 and S3 soils is reported in Table 2.

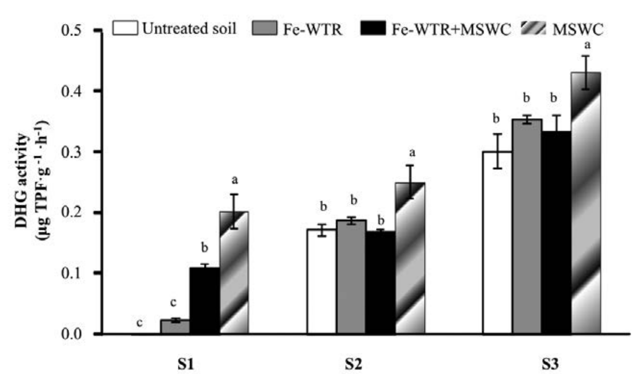

Figure 5. Dehydrogenase (DHG) activity in different untreated potentially toxic elements (PTE)-contaminated soils (S1, S2 and S3) [untreated] and in the same soils treated with water treatment residuals (WTR) at 2% (w/w), municipal solid waste compost (MSWC) at 4% (w/w) and WTR at 1% (w/w) + MSWC at 2% (w/w). For each soil, different letter on top of each bar denote statistically significant differences (Tukey-Kramer multiple comparison test; P<0.05). Data from Garau *et al.* (2019a). Total PTE content in S1, S2 and S3 soils is reported in Table 2. TPF, triphenyl formazan.

nated soils treated with different organic-based amendments (Garau *et al*., 2019a).

Evident positive effects of RM on urease activity were shown (Bhattacharyya *et al*., 2008; Garau *et al*., 2007, 2011, 2014). For instance, Garau *et al*. (2011) showed that in untreated PTE polluted soil URE activity was ~12-fold lower with respect to RM- treated soil. GLU activity on the contrary significantly decreased (*e.g*. by ~30-50% compared to the untreated soil; Garau *et al*., 2007, 2014) or was unaffected (Garau *et al*., 2011) in soils treated with RM.

Water treatment residuals

The soil microbial biomass-C remained unchanged after WTR addition (Garau *et al*., 2014), while the number of culturable heterotrophic bacteria and actinomycetes increased significantly (Garau *et al*., 2014, 2017, 2019a; Figure 4). This was explained by the greater availability in the amended soil of easily metabolisable carbon sources deriving from the OM within WTR as suggested by the significant DOC and OM increase in the amended soils (Garau *et al*., 2011, 2017). As opposed to culturable bacteria, the number of heterotrophic fungi decreased significantly after the WTR addition (Garau *et al*., 2014), while substantial increases were observed elsewhere (Garau *et al*., 2017, 2019a).

DHG increased significantly after WTR addition (*e.g*. approx. 6 and 12-fold higher at 1 and 2% amendment rate with respect to unamended soil) (Garau *et al*., 2017). However, it should be said that in this case WTR were mixed with MSWC. However, DHG increases after WTR amendment were observed in other studies (*e.g*. Garau *et al*., 2014) when null effects were also observed (Garau *et al*., 2019a; Figure 5). Also URE was stimulated in PTE-polluted soils amended with WTR (Garau *et al*., 2014, 2017, 2019a). As for RM-treated soils, GLU activity significantly decreased or was unaffected in soils treated with WTR (Garau *et al*., 2014, 2017, 2019a). This decrease appeared strongly associated with the bacteria increase in treated soils, as observed in other amended soils (Garau *et al*., 2014, 2017, 2019a).

Biochar

The influence of BCH on heterotrophic microbial communities in PTE-contaminated soil was poorly investigated so far. However, preliminary results from a recent (unpublished) study carried out in our laboratory indicated that 2.5 and 5.0% softwood-derived BCH (obtained at high pyrolysis temperature, *i.e*. 800°C; Manzano *et al*., 2020) did not change the number of culturable heteretrophic bacteria, fungi and actynomicetes in a mining soil contaminated by Pb, Cd and Zn. However, BCH obtained from different organic biomasses (*e.g*. corn cob), at lower pyrolysis temperature, *i.e*. 450°C, significantly increased soil culturable bacterial (Jiang *et al*., 2017). Such contrasting results could be explained by the different DOC content of BCH obtained at different temperatures (*i.e*. high DOC for low-temperature BCH and low DOC for high-temperature BCH; Abou Jaoude *et al*., 2020; Manzano *et al*., 2020).

Abou Jaoude *et al*. (2020), observed significant DHG increases in contaminated soils amended with low-temperature BCH supporting our previous hypothesis. For instance, DHG increased up to 49% when the polluted soil was treated with 3% (w/w) BCH. Also URE and GLU activity increased in soils treated with biochar. Particularly, the addition of 3% BCH favoured an increase of GLU of ~17% compared to the untreated control (Abou Jaoude *et al*., 2020).

Influence of municipal solid waste compost, red muds, water treatment residuals and biochar on plant growth in potentially toxic elements-contaminated soils

As previously mentioned, soil chemical, biochemical or microbial properties could be improved by amendment addition, but this does not necessarily imply a better plant growth or a reduced PTE uptake (*e.g*. Garau *et al*., 2014). For this reason, the results of several plant growth experiments can be useful to obtain a comprehensive overview of the impact of MSWC, RM, WTR and BCH on crop yield and PTE uptake in contaminated soils. The reported use of edible species (*e.g*. bean, pea, wheat and others) in these experiments is to be considered within this context and not as an agricultural option to pursue in PTE-contaminated soils (which is not permitted by any national legislation). As anticipated, such soils could be more effectively (and safely) used for non-food/feed productions allowing soil recovery and income generation.

Plant growth, estimated by root and shoot dry weight, was generally highly influenced by soil, contamination type and amendment addition, supporting the view that the amendment effectiveness needs to be evaluated case by case. Generally, adding MSWC, WTR, RM and BCH to PTE-polluted soils had a positive impact on plant growth even if some important exceptions were also reported (Castaldi *et al*., 2005, 2009b, 2018; Garau *et al*., 2017; Garau *et al*., 2020).

Municipal solid waste compost

White lupin grown in a PTE-polluted soil treated with a high rate of compost (10% w/w) showed a significantly higher biomass production with respect to untreated soil. In particular, the above ground and roots biomass increased by 3.6-fold and 1.4-fold respectively in the amended soil (Castaldi *et al*., 2005). Garau *et al*. (2017) observed that root dry weight of *H. italicum* increased by approx. 45% and 73% after amendment of a PTE-contaminated technosol with MSWC and WTR at 1% and 2% rate respectively, and very similar increases were observed for shoot dry weight. Also, *P. australis* and *A. donax* yields were significantly increased in a polluted soil (up to 22,600 mg As kg^{-1}) amended with MSWC, *i.e*. by ~41% and 67% compared to control plants (Castaldi *et al*., 2018). Root biomass of *C. cardunculus* increased by more than 17-fold and 23-fold in polluted soils amended with 2% and 4% (w/w) MSWC respectively, compared to unamended soil, while shoot biomass increased by approx. 5-fold and 10-fold (Garau *et al*., 2020).

Such positive MSWC influence on plant growth was mainly explained by its PTE-fixing abilities (as discussed previously) which greatly alleviated the toxicity of contaminated soils. However, MSWC alkalinity can also play an important role in the improvement of soil fertility (Castaldi *et al*., 2018). Finally, the increased CEC, total OM, available P and total N observed in MSWC-treated soils had a positive effect on the above-mentioned plant growth, which is overall expected in the majority of soils.

Overall, the above-mentioned plant growth effects were often accompanied by decreased PTE uptake. In addition, the highest concentrations of PTE were generally found in roots, followed by aerial parts, irrespectively of the plant species (Allende *et al*., 2014; Conesa *et al*., 2014; Bacchetta *et al*., 2015; Kouki *et al*., 2015; Pardo *et al*., 2016; Pérez-Sirvent *et al*., 2017; Castaldi *et al*., 2018). For instance, Castaldi *et al*. (2005) reported that the concentration of Pb in the aerial part of white lupin grown in a contami-

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nated compost-amended soil was 87% lower than that of control plants. Garau *et al*. (2017) reported that *H. italicum* grown in soils amended with MSWC and WTR showed approximately 50% reduction in Sb concentration in roots and shoots (*i.e.* stem + leaves). The As uptake in the below ground biomass of *P. australis* and *A. donax*, grown in a highly polluted mining soil (up to 22,600 mg kg^{-1} As) amended with MSWC, was significantly lower than that of control plants (Castaldi *et al*., 2018). However, when grown on moderately polluted soils (up to 750 mg kg^{-1} As), As uptake in the belowground biomass was unaffected or slightly increased for plants grown in MSWC-treated soils (Castaldi *et al*., 2018). By contrast, As accumulation in shoots of *P. australis* and *A. donax* grown in MSWC-amended soils was comparable and in some cases significantly lower than that observed in plants grown on control soils (Castaldi *et al*., 2018). Garau *et al*. (2020) reported a significant decrease in the concentration of different PTE in cardoon tissues grown in soil treated with 2% and 4% (w/w) MSWC. For example, As concentration in roots decreased by 11.7-fold and 8.7-fold, and Sb by 6.7-fold and 6.5-fold, in 2% and 4% (w/w) amended soils respectively, compared to control (unamended) roots. Also Cd, Cu, Pb, and Zn uptake was significantly reduced by MSWC amendment (Garau *et al*., 2020).

Red muds

The effects on plant growth of RM addition to polluted soils are contrasting based on plant species, soil type and level (and type) of contamination. Castaldi *et al*. (2009b) reported a positive effect of RM (added at 4% w/w) on pea and wheat growth in a soil polluted with Pb, Cd and Zn. In particular, the above ground biomass of pea and wheat increased by a factor of 1.8 and 5.4 respectively when RM was added to soil. However, some symptoms of leaf chlorosis (followed by necrosis) were observed for plants grown in RM-amended soil (Castaldi *et al*., 2009b). These could be ascribed to the great affinity of RM for selected elements such as phosphate, which can lead to nutrient deficiency.

By contrast, RM addition to a soil mainly contaminated by As, did not influence wheat growth, while had critical effects on bean germination which was completely inhibited (Garau *et al*., 2014). In this latter case, the RM influence on plant growth could be explained with the high salt content of the amendment, as well as with high labile As due to RM alkalinity (Garau *et al*., 2014).

Pea and wheat plants grown on a RM-amended acidic soil accumulated significantly lower amounts of Pb, Cd and Zn compared to control plants (*e.g.* <60%, 79% and 93% of Pb, Cd and Zn in pea plants grown in RM-soil with respect to control plants; Castaldi *et al*., 2009b). However, a significantly increase of As uptake (~2-fold) was observed in wheat shoots of plants grown on a RM-treated alkaline soil (Garau *et al*., 2014).

Water treatment residuals

Bean and wheat growth in the same PTE-polluted soil treated with 3% (w/w) WTR was 2.5-fold and 1.8-fold greater respectively than that of control plants (Garau *et al*., 2014). Likewise, WTR significantly promoted root and shoot growth of *A. donax and P. australis* in different PTE-contaminated soils (Castaldi *et al*., 2018), performing in some soil as well as MSWC. We already mentioned the increased yield of *H. italicum* in a technosol contaminated by Sb, Pb, Cd, and Zn, and amended with WTR+MSWC (Garau *et al*., 2017). While the observed plant growth promotion effect could not be entirely attributed to one or another amendment, this latter study indicates that MSWC and WTR can be successfully used to increase crop yield in PTE-contaminated or degraded (*i.e.* nutrient poor) soils as also supported by other authors (Clarke *et al*., 2019; Hsu and Hseu, 2011; Zhao *et al*., 2016, 2018).

As for MSWC, the increased crop yield in WTR-amended soils can be explained by a certain improvement of soil nutrient status, *i.e.* higher TOC, CEC, total P, Ca and Fe (Table 2), other than a PTE-fixing capability mainly due to its mineral components.

The addition of WTR showed some potential to reduce As uptake in roots and shoots of *A. donax and P. australis*, independently of the As concentration in soil (Castaldi *et al*., 2018). However, the uptake of As in bean shoots was significantly increased, when compared to control, when plants were grown in a WTR-amended soil (Garau *et al*., 2014).

Biochar

Despite some authors reported the phytotoxicity effects (*i.e.* inhibition of *Lepidium sativum* L. germination) of some biochars (Buss *et al*., 2016), there is increasing evidence that BCH may have a substantial role at increasing plant biomass by increasing soil fertility and reducing labile PTE in contaminated soils (*e.g.* Ibrahim *et al*., 2017; Yousaf *et al*., 2018). The latter research in particular showed that BCH can significantly stimulate bean and wheat growth while limiting the PTE uptake in plant tissues. Some (unpublished) results from our research group also indicate increased crop yield for tomato (*Solanum lycopersicum* L.) plants grown in a mining soil amended with 2.5% and 5.0% (w/w) softwood-derived BCH. Interestingly, crop yield was in the order 2.5% BCH >5.0% BCH > Control soil (no BCH added) suggesting that high BCH amounts can limit plant growth likely because of nutrient retention, as recently highlighted by Manzano *et al*. (2020).

Taken together, these results highlight an overall effectiveness of MCSW, RM, WTR and BCH at reducing PTE bioavailability and improving soil fertility in polluted soils. However, particular attention should be paid when considering RM as a potential treatment for the recovery of alkaline PTE-contaminated soils. And also, the amounts of BCH added to PTE-contaminated soils should be carefully considered to maximise plant growth and avoid soil nutrient deficiencies. Given that, as a general trend, the roots (and rhizome) of pea, wheat, bean, lupin, giant and common reed, and cardoon accumulated much more PTE than shoots (and this was often increased in treated soils), the selected amendments could be considered for their use in assisted phytostabilization protocols (Zornoza *et al*., 2002; Castaldi *et al*., 2005, 2018; Fumagalli *et al*., 2014; Garau *et al*., 2017; Gorovtsov *et al*., 2019; Garau *et al*., 2020).

Future prospects

Different prospects can be foreseen for the use of RM, MSWC, WTR and BCH in the recovery of PTE-polluted soils. For instance, their combined use has been poorly considered so far while it could provide better solutions for soil remediation. In particular, MSWC which commonly contains high DOC content could be used in combination with selected BCH able to adsorb the dissolved organic matter. This would avoid the increase of PTE solubility due to soluble DOC-PTE complex formation (Palansooriya *et al*., 2020). Likewise, the potentials of modified amendments should be better explored, *e.g.* sulphur modified BCH was very effective (more than unmodified control) at stabilizing mercury in soil (Zhao *et al*., 2020), while phosphorous-modified BCH was very active at fixing cationic and anionic PTE in soil such as Pb, Cd, Cu and As (Zhang *et al*., 2020). The possibility to use such materials

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as media for the delivery of useful microorganisms in polluted soils, *e.g*. PGPR (plant growth promoting rhizobacteria) represents another perspective to explore. Finally, it should be noted that most of the studies concerning such amendments have been carried out at the laboratory scale mostly considering short-term effects. Further long-term field studies should be necessary to fully understand the actual perspectives of these amendments in PTE polluted environments.

Conclusions

By-products generated by the municipal and industrial waste cycle such as MSWC, RM, WTR and BCH, possess valuable physico-chemical characteristics which (with few exceptions) allow their use as strategic amendments for the recovery of the fertility and functionality of PTE-contaminated soils. This is relevant, as it implies a recovery of productivity of such areas which can be devoted to the cultivation of non-food or non-feed crops. Moreover, the use of such amendments can help to reduce the disposal of some of them (*e.g*. RM) attenuating their negative environmental impact and, importantly, contributing to a circular economy.

Possible critical issues are related to the relatively high amounts added to soil (3-5% w/w in most of the studies), while the overall availability of the amendments is essentially unlimited, and their cost relatively low in relation to alternative interventions. Another issue which so far has been little addressed is the duration of the amendment effects. This is particularly important for the organic-based materials, MSWC in particular, whose stability and effectiveness could change with time due to microbial decomposition. Moreover, also plant growth over time could influence the PTE-fixing abilities of MSWC, RM, WTR and BCH, and this should be considered.

Overall, MSWC, RM, WTR and BCH can be considered as environmental friendly amendments that can contribute to the robustness of soil and plants, enhancing crop productivity in problematic and underutilized areas such those contaminated by PTE.

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