Innovative amendments derived from industrial and municipal wastes enhance plant growth and soil functions in PTE-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.

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.

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., 2009, 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, it 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; Fe₂O₃]
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 Fe₂O₃ 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 MSWC, RM, WTR and BCH**

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 to 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., 2009). 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 et al., 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) [H2AsO4-, HAsO42-] 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 m² 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 (Fe₂O₃), boehmite [AlO(OH)] and gibbsite [Al(OH)₃], while different tectosilicate-like compounds such as cancrinite [Na₆Ca₂Al₆Si₆O₂₄(CO₃)₂] and sodalite [Na₈Al₆Si₆O₂₄Cl₂] 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 limited 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., 2009). 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 (Al₂(SO₄)₃·18H₂O), ferric (e.g., FeCl₃·6H₂O) and ferrous (e.g., FeCl₂, FeSO₄·7H₂O) 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, that in the EU is regulated by Regulation (EU) 2019/1009.

BCH physico-chemical characteristics (e.g. alkalinity, high 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, -NH₂) 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 MSWC, RM, WTR and BCH 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., 2009), 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 Montenurro, 2009; 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 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 et al., 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 (H₂PO₄⁻ and HPO₄²⁻) other than toxic arsenates (H₂AsO₄⁻ and HAsO₄²⁻). 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. (2009).

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 (pHₚ𝒛𝒄) 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 pHₚ𝒛𝒄 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 pHₚ𝒛𝒄 values between ~7.0-9.0 (Kosmulski, 2016). However, this finding can not be generalized as decreases of pHₚ𝒛𝒄 were also reported after WTR
addition (Table 2).

**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 2,300 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
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 MSWC, RM, WTR and BCH on labile PTE 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. 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 PTE oxyanions**

Single step and/or sequential extraction procedures can be used to assess amendments influence on labile and potentially bioavailable As and Sb oxyanions [i.e. $\text{H}_2\text{AsO}_4^-$, $\text{HAsO}_4^{2-}$ and $\text{SbOH}_6^-$] (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 $(\text{NH}_4)_2\text{SO}_4$ solutions to
extract the non-specifically sorbed anionic PTE (Fraction 1). Then, the same soil samples are treated with NH$_4$H$_2$PO$_4$ 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$_2$O$_2$ 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 analyzed) 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.

**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 PTE in the 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$_2$EDTA 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$_2$O$_2$ 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 bio-available 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 favored: 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).

**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 (CO₃²⁻, OH⁻, PO₄³⁻) in the formation of PTE precipitates, e.g. lead carbonates [PbCO₃
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 MSWC, RM, WTR and BCH on the heterotrophic microbial community and biochemical functioning in PTE-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 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; Garau et al., 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$_2$, in PTE-contaminated soils (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., 2009; 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 $\beta$-glucosidases activity (GLU), due to extracellular enzymes involved in soil C cycle (i.e. they cleave $\beta$ 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; Garau et al., 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 $\beta$-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 waters (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-contaminated 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 heterotrophic bacteria, fungi and actinomycetes 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 MSWC, RM, WTR and BCH on plant growth in PTE-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, 2009, 2018; Garau et al., 2017; Garau et al., 2020; Garau et al., unpublished data related to BCH).

**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 contaminated 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\textsuperscript{-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\textsuperscript{-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 \textit{P. australis} and \textit{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 the 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. (2009) 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., 2009). 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., 2009). 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 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 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, such use of the selected 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 as those contaminated by PTE.

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**Table 1. Chemical characteristics of MSWC, RM, WTR and BCH*.**

| 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·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)*

| PTE | S1 Untreated | MSWC | WTR | S2 Untreated | MSWC | WTR | S3 Untreated | MSWC | WTR |
|-----|-------------|------|-----|-------------|------|-----|-------------|------|-----|
| Pb  | n.d.        | 85.00 | -   | 13.4-48.5   | 12.17-21.17 | n.d. |
| Zn  | 26.91-209   | 0.025.2 | 246.03-121.86 | n.d. |
| 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.        | n.d. |
| Sb  | n.d.        | n.d.   | n.d. | n.d.        | n.d. |
| Fe  | 5.494-22.929 | 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   | 1,709-2780  | -    | 99.48-3827 | -   |
| Mg  | 4,504-5403  | -    | 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

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**Table 2. Influence of MSWC and WTR, added at 4 and 2% (w/w) rate respectively, on selected chemical characteristics of different PTE-contaminated soils (S1, S2 and S3). Data from Manzano et al. (2016).**

|          | S1  | S2  | S3  |
|----------|-----|-----|-----|
|          | Untreated | MSWC | WTR | Untreated | MSWC | WTR | Untreated | MSWC | WTR |
| pH       |       |     |     |       |     |     |       |     |     |
| EC       |       |     |     |       |     |     |       |     |     |
| Ashes    |       |     |     |       |     |     |       |     |     |
| TOC      |       |     |     |       |     |     |       |     |     |
| DOC      |       |     |     |       |     |     |       |     |     |
| CEC      |       |     |     |       |     |     |       |     |     |
| PTE      |       |     |     |       |     |     |       |     |     |
| Pb       |       |     |     |       |     |     |       |     |     |
| Zn       |       |     |     |       |     |     |       |     |     |
| Cd       |       |     |     |       |     |     |       |     |     |
| Cu       |       |     |     |       |     |     |       |     |     |
| As       |       |     |     |       |     |     |       |     |     |
| Sb       |       |     |     |       |     |     |       |     |     |
| Fe       |       |     |     |       |     |     |       |     |     |
| Mn       |       |     |     |       |     |     |       |     |     |
| Na       |       |     |     |       |     |     |       |     |     |
| K        |       |     |     |       |     |     |       |     |     |
| Mg       |       |     |     |       |     |     |       |     |     |
| Ca       |       |     |     |       |     |     |       |     |     |

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*Accepted paper*
|                   | 3.77 | 7.87 | 4.47 | 7.58 | 7.82 | 7.46 | 8.10 | 8.22 | 7.94 |
|-------------------|------|------|------|------|------|------|------|------|------|
| pH_{H_2O}         |      |      |      |      |      |      |      |      |      |
| pH_{PCZ}          | 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(+), kg⁻¹) | 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)**

| Element | As  | Pb  | Cu  | Zn  |
|---------|-----|-----|-----|-----|
| Concentration (mg·kg⁻¹) | 22,661 | 2162 | 412 | 1535 |

Table 3. Influence of RM, added at 4% (w/w) rate, on selected chemical characteristics of an acidic PTE-contaminated soil. Data from Garau et al. (2014).

|                                | Untreated soil | RM-soil     |
|--------------------------------|----------------|-------------|
| pH_{H2O}                       | 6.84           | 8.80        |
| Electric conductivity (mS 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      |
Table 4. Influence of a softwood-derived BCH on physico-chemical characteristics of the different PTE-polluted soils. Data from Manzano et al. (2020).

| 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  |
Figure 1. Water soluble and exchangeable As fractions extracted from an untreated and a RM-treated PTE-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).
Figure 2. Water soluble Cd, Zn and Pb fractions extracted from an untreated PTE-polluted soil and from the same soil treated with 2 and 4% (w/w) 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 LSD test; \( P<0.05 \)). Data from Garau M et al. (2019).
Figure 3. Water soluble Cd, Cu, Pb and Zn extracted from an untreated PTE-polluted soil and from the same soil treated with 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 LSD test; $P<0.05$). Data from Garau et al. (2014).
Figure 4. Total culturable heterotrophic bacteria in different untreated PTE-contaminated soils (S1, S2 and S3) [untreated] and in the same soils treated with WTR at 2% (w/w), WTR at 1% (w/w) + 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 G et al. (2019). Total PTE content in S1, S2 and S3 soils is reported in Table 2.
Dehydrogenase (DHG) activity in different untreated PTE-contaminated soils (S1, S2 and S3) [untreated] and in the same soils treated with WTR at 2% (w/w), 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 G et al. (2019). Total PTE content in S1, S2 and S3 soils is reported in Table 2.

|          | S1             | S2             | S3             |
|----------|----------------|----------------|----------------|
| Untreated | Fe-WTR         | Fe-WTR+MSWC    | MSWC           |
| DHG activity (µg TPF·g⁻¹·h⁻¹) |                |                |                |
| Untreated soil | 0.0 ± 0.0      | 0.0 ± 0.0      | 0.0 ± 0.0      |
| Fe-WTR    | 0.1 ± 0.1      | 0.2 ± 0.2      | 0.3 ± 0.3      |
| Fe-WTR+MSWC | 0.4 ± 0.4     | 0.5 ± 0.5      | 0.6 ± 0.6      |
| MSWC      | 0.7 ± 0.7      | 0.8 ± 0.8      | 0.9 ± 0.9      |

Figure 5. Dehydrogenase (DHG) activity in different untreated PTE-contaminated soils (S1, S2 and S3) [untreated] and in the same soils treated with WTR at 2% (w/w), 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 G et al. (2019). Total PTE content in S1, S2 and S3 soils is reported in Table 2.