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Mutual effect of *Phragmites australis, Arundo donax* and immobilization agents on arsenic and trace metals phytostabilization in polluted soils

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A R T I C L E I N F O

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A B S T R A C T

This study assessed the suitability of *Phragmites australis* and *Arundo donax* for the aided phytostabilization of metal(loid)s in polluted soils treated with an iron-rich water treatment residue (Fe-WTR), a municipal solid waste compost (MSW-C) and their combination (Fe-WTR + MSW-C). The three soils under study (S1, S2, S3) showed very high total concentrations of As (from 371 to 22,661 $mg \cdot kg^{-1}$ d.w.) and variable amounts of co-occurring trace metals (TMs) (i.e. Pb, 74–2162; Zn, 57-1535 and Cu, 19–412 $mg \cdot kg^{-1}$ d.w.). Results showed that *P. australis* and *A. donax* biomass was significantly increased in all the amended soils and followed the order: MSW-C > Fe-WTR + MSW-C > Fe-WTR > Control. For both plant species grown in the amended soils, metal(loid)s concentration in below ground organs were higher than those in above ground tissues. In S1 soil (the most polluted and acidic; pH 3.77), the highest As bioaccumulation factors (BAFs) were recorded for plants grown on untreated soil (approx. 45% higher with respect to those recorded for plants in treated soils), where the concentration of labile As was significantly higher with respect to amended soils. By contrast, in S2 and S3 soils, the most effective As bioaccumulator plants were grown on soils treated with compost, even if the addition of this amendment induced a decrease of the soil As extractability. Similar results were detected for TMs in S1 soil, where *P. australis* and *A. donax* grown on soil amended with compost showed the highest Pb, Zn and Cu BAFs, while variable results were detected in S2 soil. The lowest As translocation factors (TFs ≪1.0) were detected for plants grown on compost-amended soils (25 and 51, 34 and 50, 64 and 55% lower with respect to *P. australis* and *A. donax* control plants in S1, S2 and S3 soils respectively), while TMs translocation from roots to shoots was more variable and depending on soil, TMs, amendment and plant species.

Overall, our results indicate the suitability of *P. australis* and *A. donax*, and of Fe-WTR and MSW-C, for the aided phytostabilization of soils contaminated with arsenic and trace metals.

1. Introduction

Mining, which is considered one of the most impacting anthropogenic land use, is one of the major environmental source of metal(loid)s (e.g. As, Pb, Cu and Zn) whose combined presence in primary sulfide ores is quite common (Manzano et al., 2016; Pérez-Sirvent et al., 2017). In the absence of effective recovery and securing interventions, the abandonment of mining sites can cause severe pollution events involving large areas or entire regions (Castaldi et al., 2005; Mele et al., 2015; Garau et al., 2017). Most often, this is due to the spread of contaminants from mine tailings and flotation sludge, both containing critical amounts of metal(loid)s (Castaldi et al., 2005; Pérez-Sirvent et al., 2017). As a result, polluted sites commonly exhibit unfavorable conditions for plant growth and soil functionality, such as very low pH values, high concentrations of toxic metal(loid)s in labile form, low levels of nutrients and poor soil structure (Ashraf et al., 2011; Bacchetta et al., 2015).

In the last decades, a great deal of attention has been put on the evaluation of novel and less impacting strategies for the remediation of metal(loid)-contaminated soils (Mench et al., 2006; Garau et al., 2014; Quintela-Sabarís et al., 2017). One such approach is based on the in-situ chemical immobilization of the contaminants using different sorbent materials, e.g. compost, Fe-oxides, zeolites, biochar, lime etc. (e.g. Castaldi et al., 2005; Garau et al., 2007; Fellet et al., 2014; Yang et al., 2016; Zhang et al., 2016; Moreno-Barriga et al., 2017; Garau et al., 2017). Ideally, these amendments should be able to reduce the

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concentration of labile and bioavailable contaminants by sorption and/or (co)precipitation reactions (Basta and McGowen, 2004; Castaldi et al., 2005; Manzano et al., 2016; Garau et al., 2017), and/or to change the speciation of the dissolved metal(loid)s (Beesley and Marmiroli, 2011), thereby improving the soil physico-chemical and biological attributes (e.g. pH, cation exchange capacity, nutrient supply, microbial abundance, diversity and functionality) (Garau et al., 2014; Bacchetta et al., 2015).

Also plant communities can significantly contribute to mitigate the adverse effects of critical metal(loid) concentrations in soil. Plants can limit the leaching of contaminants to ground water, the erosion of the polluted soil and the contamination of surface water, thus preventing the spread of contaminants and favoring soil biological recovery in polluted areas (Castaldi et al., 2009; Ashraf et al., 2011). Therefore, a combined approach employing both sorbents with suitable metal(loid)-immobilizing abilities, and plant species able to further stabilize labile contaminants in soil, should be ideal in order to maximize the effectiveness of the remediation intervention (Fellet et al., 2014; Moreno-Barriga et al., 2017).

The plant ability to limit the spread of contaminants, and promote the recovery of polluted soil, is the basis of phytostabilization. This is a phytoremediation approach through which labile pollutants are immobilized below ground in soil and/or within roots, thus reducing the metal(loid)s impact on the ecosystem and minimizing their entry into the food chain (Baker et al., 1994; Wong, 2003; Weis and Weis, 2004; Bonanno, 2011; Bacchetta et al., 2015). The extent of metal(loid) uptake by the plant can vary largely among plant species and depends also on the metal(loid) concentration, mobility and speciation, as well as on the soil properties, which in turn can be affected by the amendment addition (Bonanno, 2011; Kouki et al., 2015).

Many wetland and riparian plant species display well recognized metal(loid)s bioaccumulation properties, high tolerance to both low soil pH and high concentrations of Pb, Cd, Cu, Zn, and As, which are preferentially accumulated in the root/rhizome system with very little translocation to the above ground tissues (Bragato et al., 2006; Grisey et al., 2012; Guo et al., 2014; Pardo et al., 2016; Vymazal, 2016; Pérez-Sirvent et al., 2017). This is the case of the helophytes *Phragmites australis* (Cav.) Trin. ex Steud (common reed), and *Arundo donax* L. (giant reed), two perennial herbaceous species that can form dense monospecific stands, respectively in wetlands with superficial stagnant water and muddy sediment (e.g. Bonanno, 2011, 2013) and in riparian sites. Several studies demonstrated the ability of *P. australis* and *A. donax* to grow on metal-contaminated mine tailings and soils (Batty and Younger, 2004; Bacchetta et al., 2015; Kouki et al., 2015; Oustriere et al., 2017; Wang and Jia, 2017) and concentrate toxic chemicals in below ground organs with no appreciable harm to their own growth and development (Mirza et al., 2011; Alshaal et al., 2013; Oustriere et al., 2017). However, the effectiveness of both species in the phytostabilization of As and TMs co-contaminated soils has never been tested before, as well as the potential role of soil amendments on the phytostabilization performance. Remediation of As and TMs co-contaminated soils can be very challenging due to the different chemical nature of the contaminants which commonly show contrasting behaviors in soil: e.g. TMs are generally present in soil as divalent cations, while As is mostly found either in neutral (arsenite) or anionic (arsenate) form. Combining phytostabilization with the addition to soil of selected amendments could therefore represent a successful strategy for the recovery of multielement-polluted soils.

In a previous study, we evaluated the influence of different municipal solid wastes, i.e. an iron-rich water treatment residual (Fe-WTR), a municipal solid waste compost (MSW-C) and their combination (Fe-WTR + MSW-C), on the mobility of As and co-occurring TMs (i.e. Pb, Cu and Zn) in three different polluted soils (Manzano et al., 2016). In the present work, which is a follow-up research of our previous study (Manzano et al., 2016), we used the same amended polluted soils to test the effectiveness of an aided phytostabilization approach based on the separate growing of *P. australis* and *A. donax* for 18 months. In this regard, it should be mentioned that most studies addressing this issue, typically involved short-term laboratory experiments (e.g. Stoltz and Greger, 2002; Guo et al., 2014; Bacchetta et al., 2015; Pérez-Sirvent et al., 2017), while long-term cultivation experiments are rare or missing at all.

The two plant species were selected taking into account their ability to spread by vegetative growth originating large clonal stands and the different ecological requirements in terms of water availability (Packer et al., 2017), that gives the possibility to consider their combined used in areas where varying water availability in the soil may be a limiting factor.

The aim of the present study was therefore to evaluate the feasibility of using *P. australis* and *A. donax* in combination with selected amendments, i.e. Fe-WTR and MSW-C, for the aided phytostabilization of As and TMs co-contaminated soils.

To this end, the growth of *P. australis* and *A. donax* in the polluted amended soils was investigated and the metal(loid)s uptake and distribution in the different organs of the plant (i.e. roots, rhizome and shoots) were determined. The metal(loid) bioconcentration and translocation factors of *P. australis* and *A. donax* grown in the differently amended soils were also calculated to infer the relevance for phytostabilzation of the plant/amendment combination.

2. Materials and methods

2.1. Experimental set-up, soil and plant analyses

Common reed and giant reed clonal ramets were grown in a pot experiment using three different contaminated soils (S1, S2, S3) which were separately amended with Fe-WTR (2% w/w), MSW-C (4% w/w) and Fe-WTR + MSW-C (1% w/w + 2% w/w respectively). These rates were selected based on the metal(loid)s immobilizing capabilities of the Fe-WTRs and MSWC employed in this study when applied to different contaminated soils (Mele et al., 2015; Garau et al., 2014). *P. australis* was collected from a natural site in North Sardinia (Italy) and vegetatively propagated. A commercial clone of *A. donax* was provided by the Italian nursery Arundo Italia. Plants grown in contaminated untreated soils were also included as control. The pot experiment was carried out at the University of Sassari agricultural lab and farm of “Surigheddu” (Alghero, Italy). The soils and amendments used in the pot experiment have been extensively described in our earlier study in which the effectiveness of Fe-WTR, MSW-C and their combination, as metal(loid)s immobilizing agents, was determined (Manzano et al., 2016).

Briefly, the contaminated soils were collected in the vicinity of an ancient mine located in the Sarrabus-Gerrei mining district, in the municipality of “Salto di Quirra” (SE Sardinia, Italy). The mining sulfide deposit occurs in a Cambrian to Devonian volcano-sedimentary sequence mainly consisting of black phyllitic shales, grey shales, phyllites, metasandstones, metarhyolites and metarhyodacites, associated with late Hercynian magmatic products such as dioritic porphyrites and lamprophyres in dikes (Frau and Ardau, 2003). Primary metalliferous mineralization is composed of arsenopyrite and galena and minor amounts of sphalerite, pyrite, chalcopyrite and pyrrhotite; gangue minerals are mainly quartz, minor calcite and siderite, and rare fluorite.

Fe-WTR and MSW-C were provided by the Public limited company Abbanoa S.p.A. (Sardinia, Italy) and the Plant Secit Facility S.p.A. Consorzio Zir (Chilivani-Ozieri, Sardinia, Italy), respectively. Before addition to the polluted soils, Fe-WTR and MSW-C were dried at 105 °C for 48 h, finely ground and sieved to < 2 mm. The Fe-WTR and MSW-C had approximately neutral and sub-alkaline pH (7.15 and 7.93 respectively), with electrical conductivities of 1.2 and 3.3 mS cm^{-1}, pH_{PZC} values of 6.7 and 5.6, and organic matter contents of 14.5 and 27.3% (*w*/w), respectively. Humic and fulvic acids accounted for 2.7 and 15.3% (w/w) of Fe-WTR and MSW-C respectively (Castaldi et al., 2017; Silvetti et al., 2017).