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Effect of biochar amendments on As and Pb mobility and phytoavailability in contaminated mine technosols phytoremediated by *Salix*

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ABSTRACT

Mining activities lead to widespread environmental pollution of terrestrial ecosystems due to the presence of metal(loid)s in tailings. These contaminated areas present a health risk and hence need to be rehabilitated. *Ex situ* methods for soil remediation have been used for a long time but are expensive and disruptive to soil. Phytoremediation techniques for the stabilization or extraction of metal(loid)s could be an efficient alternative as they provide a low-cost and environmentally friendly option. However, due to the often poor nutrient content of these contaminated soils, amendments must be added to enhance plant growth and to improve phytoremediation efficiency. Biochar, a pyrogenic product, is a promising amendment for assisted phytoremediation. The aims of our study were (i) to evaluate the effect of a pinewood biochar on the physicochemical properties of a former mine contaminated technosol, (ii) to assess the mobility and phytoavailability of As and Pb and (iii) to investigate the remediation potential of three willow species (*Salix alba*, *Salix viminalis* and *Salix purpurea*). A greenhouse experiment was conducted with contaminated technosols amended with biochar and garden soil, single or combined, revegetated with the 3 willow species. The physicochemical properties of soil pore water (SPW) as well as metal(loid) concentrations were determined. Plant growth, *Salix* organ dry weight and metal(loid) uptake were determined in order to evaluate the phytoremediation potential of the three *Salix* species studied. Biochar increased the pH and electrical conductivity of SPW. Biochar addition had no effect on As mobility but decreased SPW Pb concentration by 70%. For the three *Salix* species investigated, biochar addition to the polluted soil induced a better growth and a higher dry weight production. In most modalities tested, the metal(loid) content in the *Salix* organs increased due to the biochar application. Globally, a positive effect of biochar was noticed on the soil qualities (pH and electrical conductivity increase) and plant growth. Metal(loid)s were mostly confined to the roots. Among the species tested, *Salix alba* presented the lowest metal(loid) concentrations in the aerial parts, making it a particularly suitable tool for Pb soil phytostabilization.

1. Introduction

Potential toxic elements (PTE) such as metal(loid)s are naturally present in the environment at rather low concentrations. However, since the beginning of the industrial era, and due to anthropogenic activities such as mining and smelting, contamination by PTEs has increased drastically. The number of sites potentially contaminated in Europe is estimated at 3.5 million (Petruzelli, 2012). In addition, PTEs do not remain fixed and stabilized on site but can be disseminated to the surrounding environment by wind erosion and to the ground and surface water through leaching and run-off/on (Puga et al., 2016) and consequently they can enter the food chain (Kloss et al., 2014). Metal(loid) contaminants are therefore a major issue, not only for the environment but also for human health (Ali et al., 2013). As a result, remediation of these polluted sites has become an important societal objective.

Physical and chemical techniques to remediate contaminated soils have been used for a long time, but these conventional methods have many flaws: they are expensive, difficult to implement and disruptive to soil (Ali et al., 2013). An alternative is phytoremediation, defined as the use of plants to remediate polluted soils. It is performed *in situ* to stabilize or to extract soil pollutants (Moosavi and Seghatoleslami, 2013). Phytoremediation uses mainly solar energy (Borišev et al., 2009), and maintains or can even improve soil structure (Mleczek et al., 2010). Briefly, due to its capacity to install a plant cover which (i) limits

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Abbreviations: PTE, potential toxic element; SPW, soil pore water; EC, electrical conductivity; DOC, dissolved organic carbon.

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erosion, (ii) creates an aerobic environment in the rhizosphere, (iii) provides organic matter in the soil, and (iv) aggregates and binds metal(loid)s to soil components, it is perceived as an environmentally friendly method (Vamerali et al., 2009; Ali et al., 2013). However, when PTE soil concentrations are very high, phytoextraction will take decades and poses the problem of PTEs returning to the ground when leaves and branches are shed. For this reason, phytostabilization, which strongly constrains these pollutants in soil and in the plant root system without translocation to the harvestable parts, is an efficient alternative.

To improve phytoremediation and because contaminated soils are often poor in available nutrients and often acidic for plants and the associated microbiota, organic and/or inorganic amendments must be used (Park et al., 2011). Moreover, when added to soil these amendments can contribute by their own properties to reducing contaminant levels in water soil solution, by reducing PTE leaching (Melo et al., 2016). Furthermore, Agegnehu et al. (2015) demonstrated that two organic amendments (biochar and compost) improved peanut seed and pot yields, as well as the chlorophyll contents of plants. These positive effects are associated to a better C, N, P, K plant uptake and to an increase in soil soluble organic carbon availability. Biochar is one of these organic amendments, resulting from the pyrolysis of organic materials under limiting oxygen conditions (Anawar et al., 2015). It is a porous, carboneous product characterized by a large surface area, a low density, a high cation exchange capacity (CEC), an alkaline pH (Paz-Ferreiro et al., 2014) and usually lasts longer than other amendments. Its beneficial use in agronomy has been known for a long time (*cf.* Terra Petra) (Lehmann and Joseph, 2009). Moreover, Fellet et al. (2011), Beesley and Marmiroli (2011) and Zhang et al. (2013) demonstrated the effectiveness of biochar to remediate PTE contaminated mine soils by reducing their concentrations in soil pore water and in the plants grown in the amended soils.

>400 plant species, either associated with amendments or not, have proved to be efficient phytoremediators (Moosavi and Seghatoleslami, 2013). Among them, a few Brassicaceae have been described as PTE hyperaccumulators (Sarma, 2011). However, their low biomass and slow growth rate diminish their potential use in phytoremediation (Ghosh and Singh, 2005). To overcome these drawbacks, tree species, which present a rapid growth, a large biomass production, a deep root system and sometimes a high accumulation capacity for PTEs, are interesting phytoremediation options. Among woody species, Salicaceae have already been proposed as phytoremediator plants (Marmiroli et al., 2011). Indeed, Bart et al. (2016) demonstrated the capacity of *Salix viminalis* and *Salix purpurea* to grow on a mine soil contaminated by As, Pb and Sb.

In order to remediate a multi-PTE contaminated soil using assisted phytoremediation, the goals of our study were to investigate the effect of two organic amendments, a garden soil and a pinewood biochar, single or in combination, on i) the physicochemical properties of a multi-contaminated soil and ii) the growth and metal(loid) uptake by three willow species (*Salix alba*, *Salix viminalis* and *Salix purpurea*). To our knowledge, this paper is the first study describing the effect of biochar on the remediation capacities of willow species towards an acidic and highly multi-contaminated PTE soil.

2. Materials and methods

2.1. Study site

The study focused on a technosol derived from a former silver-lead mine extraction site located in Pontgibaud, Puy-de-Dôme, Auvergne, France. It was one of the largest mining and metallurgical districts in Europe during the nineteenth century but has been disused since 1897. Due to the mining activities, the site is an acidic sandy soil contaminated mostly by high concentrations of arsenic ($539.06 \pm 0.01\ \mathrm{mg \cdot kg^{-1}}$) and lead ($11{,}453.63 \pm 0.18\ \mathrm{mg \cdot kg^{-1}}$) (Cottard, 2010). Soil samples were collected in a settling pond (between 0 and 20 cm of depth) in the area called Roure-les-Rosiers (GPS coordinates: 45°49′59″ North and 2°51′04″ East).

2.2. Amendments

Two different organic amendments, single or combined, were used: i) a garden soil collected in the park of Orleans University, France; ii) biochar, produced from pinewood woody biomass (VT Green Company, Saint Bonnet de Rochefort, France). The main physico-chemical properties and total PTE concentrations in the biochar are presented in Table 1.

2.3. Soil mixtures preparation

Three different 2 mm diameter sieve soils were prepared: i) Garden soil (named G, control soil), ii) Pontgibaud technosol (named P) and iii) a mixture of 50% Technosol and 50% Garden soil (v/v) (named PG). These three soils were amended with 0%, 2% or 5% (w/w) biochar and placed in plastic pots (87 × 113 mm). Six pots were prepared per modality and per *Salix* species tested. Potted soils were allowed to equilibrate 5 days at field capacity using tap water before the introduction of non-rooted *Salix* cuttings (T0).

2.4. Technosol analysis

pH and EC of the different technosols were measured using a pH meter (FE20/EL20, Mettler-Toledo AG 2007) and a multimeter (WTW Multi 1970i, GEOTECH, Denver, Colorado) according to the following protocol: 10 g of technosol were put in solution with 25 mL distilled water, the solutions were stirred during 1 h (150 rpm), then left to settle for half an hour before measurements were made.

Table 1
Main biochar physico-chemical properties provided by VT Green.

Parameter	Value	Unit
pH	82	
Conductivity	9	mS/cm
Resistivity	115,207	Ohm cm
Density without compaction	0.125	kg/L
Density with compaction	0.167	kg/L
Water-insoluble	85.2	%
Insoluble in acid	84.8	%
Total exchange capacity	46	Me/kg
total porosity	96	%
Water retention capacity	85	%v/v
Retention capacity for air	11	%v/v
Major elements secondary		
Total nitrogen	<0.20	%
Total organic carbon	73.7	%
Mineral materials	1.27	%
Lost on ignition at 450 °C	89.0	%
P_2O_5 total (soluble in mineral acids)	<0.07	%
P_2O_5 soil. water%	<0.20	%
K_2O	0.14	%
K_2O water soluble	0.06	%
Total CaO	0.36	%
Total MgO	0.10	%
Total Na_2O	<0.03	%
Total sulfur	<0.10	%
Trace elements		
Total arsenic	<0.50	mg/kg
Total cadmium	0.050	mg/kg
Total chrome	16.5	mg/kg
Total cobalt	0.54	mg/kg
Total mercury	0.004	mg/kg
Total molybdenum	0.62	mg/kg
Total nickel	11.1	mg/kg
Total lead	2.36	mg/kg
Total selenium	<1	mg/kg

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