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The reduction of the As and Pb phytotoxicity of a former mine technosol depends on the amendment type and properties.

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Abstract

In remediation of metal(loid) polluted soils, it is crucial to improve soil conditions and reduce metal(loid) toxicity to permit plant growth. To do that, amendments, such as biochar, activated carbon, and redmud, can be applied to the soil. Their effects are dependent on their type and properties. The aims of this study were thus to evaluate the potential of diverse biochars, activated carbons, and redmuds to reduce phytotoxicity of a former mine technosol polluted with As and Pb. Two pots experiments were set up. The first one applied on Pontgibaud technosol ten biochars, eight activated carbons, and three redmuds, at 2% for the biochars and activated carbons and 1% for the redmud. Soil pore water properties (pH, electrical conductivity), metal(loid) mobility, and *Phaseolus vulgaris* growth were monitored. In a second experiment, the five best amendments, one redmud associated with two biochars and two activated carbons, selected based on their ability to improve soil conditions, immobilize metal(loid)s and improve plant growth, were applied. The same plant species was used and soil and plant parameters were measured. Results demonstrated that not all amendments were capable of ameliorating soil conditions and reducing soil phytotoxicity. Moreover, the five selected amendments (biochars from oak bark sapwood and bamboo, activated carbons from vegetal feedstock chemically activated and physically activated, modified redmud) showed good sorption capacity towards Pb, with maximum sorption capacity between 63 and 217 mg.g^{-1}, depending on the amendment, and their combined application led to better soil properties improvement than the single amendments. However, plant growth was only ameliorated further than a single application in the redmud-biochar combination but not in the association of redmud with activated carbon. This study is one of the first to deliver a rapid phytotoxicity test screening demonstrating that redmud associated with particular biochar could be beneficial in reducing the phytotoxicity of technosol polluted with As and Pb and thus allow plant growth and a phytomanagement process.

Keywords

Activated carbon, Biochar, Metal(loid)s, Phytotoxicity test, Redmud

Introduction

Soil is essential for human life: it provides several ecosystem services such as carbon storage, water regulation, food production, nutrient cycling, (micro)organism habitats and spare-time activities (Kopittke et al., 2019; Neina, 2019). However, with the industrialization and expanse of the human population, soils are degraded and are thus unable to fully provide their services. One important soil degradation of anthropogenic origin is soil contamination resulting from mining activities. The tailing wastes produced during the extraction process are usually fine-grained and contain residual concentrations of metal(loid)s. Such high metal(loid) levels and extreme soil properties (acidic pH, low organic matter, and nutrient contents) prevent plant development on those materials, which are thus subjected to wind erosion, endangering the surrounding area (Ghosh and Maiti, 2020; Karaca et al., 2018). Moreover, metal(loid)s of anthropogenic origin are more mobile than the ones from natural sources, and thus they are easily leached during rain events; thus metal(loid)s can be found in the rivers boarding contaminated sites. In addition to the reduction of soil fertility, metal(loid)s, which cannot be broken down and thus accumulate in soils, are toxic to human health (Briffa et al., 2020).

Over the last few years, phytomanagement has gathered research attention as a way how to remediate polluted areas. Phytomanagement is a combination of two goals. The first one is to reduce the toxic effects that polluted soils induce on human health and the environment; the second is to generate a valuable biomass (Burges et al., 2018). However, for plants to establish on such highly contaminated sites, two difficulties must be raised: (i) soil toxicity needs to be reduced, especially the metal(loid) bioavailability and concentrations in the interstitial water must be lowered; and (ii) fertility must be improved. These two points can be met by the application of amendments. Diverse organic and inorganic amendments can be applied but three attracted attentions over the last decade: redmud, biochar, and activated carbon. Redmud is the by-product of alumina production. It is characterized by a fine grained texture, an alkaline pH and a large surface area (Hua et al., 2017; Khairul et al., 2019). Biochar is a carbonaceous material produced from the pyrolysis of biomass. It is characterized by a high carbon content, an alkaline pH, a large surface area, and an elevated water holding capacity. A large panel of biomass can be used as feedstock for biochar production. Indeed, biochar properties will depend on the feedstock used and the pyrolysis conditions (Ghosh and Maiti, 2020; Guo et al., 2020; Kumpiene et al., 2019). Finally, activated carbon is a product obtained in the same way as the biochar and subjected, during or after pyrolysis, to a physical or chemical activation, with the goal of improving its properties and thus its effects on soil (Wang and Wang, 2019). Previous studies demonstrated the potential of these amendments in phytoremediation. For instance, Egene et al., (2018) demonstrated that biochar was capable of stabilizing Pb and Zn, while (Lebrun et al., 2018a) showed that biochar capacity to immobilize metal(loid) and improved willow growth depended on the biochar particle size. Biochars made from manure immobilized pollutants in mine soils and improve *Brassica napus* growth (Cárdenas-Aguiar et al., 2020; Gascó et al., 2019). Similarly, diverse activated carbons applied to contaminated soil were able to immobilize Cd (Liu et al., 2018). Finally, stabilization of both metals and metalloids was observed after redmud application to contaminated soil (Bertocchi et al., 2006). These studies demonstrated the potential of biochar, activated carbon, and redmud to stabilize metal(loid), and improve plant growth, therefore enhancing phytoremediation efficiency.

Moreover, amendments could be applied in combination to potentially cumulate the effects obtained individually. For instance, biochar is very effective for the immobilization of cations such as Pb but less efficient for anions like As; whereas redmuds were shown efficient for As immobilization (Feigl et al., 2012; Lebrun et al., 2019).

The goal of this study was to evaluate, using a phytotoxicity test with *Phaseolus vulgaris*, the effect of several biochars, activated carbons, and redmuds on the soil physicochemical properties, metal(loid) immobilization, and *Phaseolus vulgaris* growth, used as a bio-indicator plant. Based on the results of the first experiment, five amendments were selected; the selected redmud was combined with either biochar or activated carbon. The second experiment aimed to evaluate the effects of redmud associated with biochars or activated carbons on the physicochemical properties of the soil, the stabilization and reduction of the toxicity of metal(loid)s, and plant growth. *In fine*, the purpose was to determine which amendments were efficient for metal(loid) toxicity decrease in soil. For both phytotoxicity tests, *Phaseolus vulgaris* was used as the bio-indicator. Indeed, it is very responsive to the change in soil growing conditions, and its growth is related to metal(loid) toxicity (Kumpiene et al., 2017; Lebrun et al., 2018b). To the best of our knowledge, it is one of the first studies providing a rapid screening, using a bio-indicator plant, to determine the best amendments capable of reducing metal(loid) toxicity in soil.

Materials and Methods

1. Site description

The soil was collected on the former mine site of Pontgibaud (Auvergne-Rhones-Alpes, France). This silver-lead extraction mine was very active until the nineteenth century. Such intense activity produced huge amounts of wastes highly contaminated with arsenic and lead. Previous studies showed that this mine technosol had an acidic pH, a low organic matter content, reduced nutrient availability, and high total As and Pb concentrations: 1501 mg.kg^{-1} As and 19228 mg.kg^{-1} Pb, which is 75 and 64 times above maximum permissible limits (Ashraf et al., 2019; Lebrun et al., 2019; Manhattan Lebrun et al., 2021c).

2. Amendments used and characterization

Three amendment types were used in this study: biochar, activated carbon, and redmud.

Ten biochars were tested; they were made from six feedstocks: hardwood (two biochars), oak-bark sapwood (two biochars), pine bark (three biochars), coconut (one biochar), bamboo (one biochar), and P*seudotsuga* (one biochar). The two biochars made from hardwood biomass harbored two particle sizes: 0.5-1 mm, and 1-2.5 mm. Similarly, the first biochar made from oak bark sapwood had a particle size of 0.2-0.4 mm, while that of the second one was 0.5-1 mm. The particle sizes of the three pine bark biochars were: 0.2-0.4 mm, 0.5-1 mm and 1-2.5 mm. All the biochars were provided by La Carbonerie (Crissey, France), except for the coconut biochar that was provided by Jacobi Carbons (Paris, France) and the *Pseudotsuga* biochar, impregnated with arbuscular endomycorrhizal fungus (*Glomus intraradices* at 50 units/g), which was a commercial product (SylvaFertilis, Caen, France). The pyrolysis conditions of the biochar provided by La Carbonerie were: residence time of 3 h, a heating rate of 2.5 °C.min^{-1} , and temperature of 500 °C. Unfortunately, no production information could be obtained for the other two biochars.

The eight activated carbons tested were all provided by Jacobi Carbons (Paris, France) and were made of either vegetal or mineral feedstock. Activation was performed either with steam or a chemical agent.

Finally, three redmuds were used: one was an ochre sampled from the charcoal mine of Ales (France) while the other two were provided by Alteo Environnement (Gardanne, France). The first commercial product was the Bauxaline and the second one was a neutralized Bauxaline.

The amendments were characterized for their pH, electrical conductivity (EC), redox potential (Eh), specific surface area, total pore volume, pore diameter, and C, H, and N contents, using the following methods: (i) pH, EC and Eh were measured with a multimeter (Seven Excellence, Mettler Toledo, USA) after a 4-hour agitation of 1:7 amendment: water ratio (Lebrun et al., 2018b); (ii) specific surface area, total pore volume and pore diameter were measured by the BET method (Lebrun et al., 2018b), and (iii) C, H, and N contents were determined using a Flash 2000 organic elemental analyzer (Thermo) (Manhattan Lebrun et al., 2021b). The amendment codes and descriptions are given in Table S1.

3. First phytotoxicity test using amendments alone

A first phytotoxicity test was set up in order to select amendments with the best results in regards to soil pore water. In this phytotoxicity test, all the amendments were added individually to the technosol of Pontgibaud: biochars and activated carbons were added at 2 % (w/w) and the redmuds at 1 % (w/w). These concentrations were based on previous studies performed which found amendment effects at those doses (Lebrun et al., 2020; Manhattan Lebrun et al., 2021c, 2021a). In addition, a treatment without any amendment was implemented as a control. Treatment codes and descriptions are given in Table 1.

The substrates prepared were put in 0.5 L pots, four replicates were made for each treatment. The substrates were let to equilibrate for two weeks before introducing *Phaseolus vulgaris* seeds. The plants were grown for 15 days under greenhouse conditions: 20 °C temperature, 16 h light.

During the experiment, soil pore waters (SPWs) were sampled three times: just after substrate preparation (T0), at sowing time (T14), and at harvest time (T29). The sampling was made using soil moisture samplers (Rhizon®, model MOM, Rhizosphere Research Products, Wageningen, The

Netherlands), placed at 40° inside each pot. The pots were saturated with water the day before sampling and SPWs were sampled under vacuum. The SPW samples were used directly to measure pH and EC using a multimeter (Seven Excellence, Mettler Toledo, USA) and then acidified to measure As and Pb concentrations using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) (ULTIMA, Horiba, San Francisco, USA).

After 15 days of growth (T29), *Phaseolus vulgaris* plants were harvested. The leaves, stems, and root parts of the plants were separated and washed. After 72 h of drying at 60 °C, dry weight (DW) was determined.

Based on the results of this first phytotoxicity test (showed in the Results section), five amendments were selected for the second test: two biochars, two activated carbons, and one redmud.

4. Second phytotoxicity test using amendments combined

In the second phytotoxicity test, the five amendments selected from experiment 1 were combined. The five amendments were: bamboo biochar (BA), oak bark sapwood biochar (BS2), activated carbons EK5 (vegetal feedstock, steam activation), and L27 (vegetal feedstock, chemical activation), and the modified Bauxaline redmud (RMM).

The redmud was added at 1 % (w/w) in association with either biochar or activated carbon added at 2 % (w/w), the same doses applied in the first test. Five pots (0.5 L) were prepared for each treatment and a control with only Pontgibaud technosol was also prepared. After a two-week equilibration period, *Phaseolus vulgaris* was sown.

Similar to the first experiment, SPWs were sampled at the beginning of the experiment (T0), and at the end (TF), the same analyses were undertaken. After 15 days, plants were harvested and analyzed for biomass production.

5. Sorption tests

The sorption capacity of the five amendments used in the second experiment was measured towards Pb, the most important contaminant of the Pontgibaud technosol. Pb is highly toxic and has a higher solubility than As in the soil (Lebrun et al., 2017).

For this, 0.1 g of the amendment was mixed with 10 mL of a Pb (in the form of $PbNO_3$) solution at 0.1, 0.5, 1, 1.5, 2, and 2.5 g.L^{-1}. The mixtures were then agitated (150 rpm) for 24 h at room temperature. Solutions were filtrated and pH was measured. After acidification, Pb concentration was measured by ICP-AES.

The amount of Pb sorbed (Qe) onto the amendment was calculated using equation (1):

$$(1)\ \mathrm{Qe} = \frac{(\mathrm{Ci} - \mathrm{Ce})\mathrm{V}}{\mathrm{m}}$$

With Qe the amount of Pb sorbed (mg.g^{-1}), Ci the initial Pb concentration (mg.L^{-1}), Ce the Pb concentration at equilibrium (mg.L^{-1}), V the volume tested (10 mL), and m the mass of the amendment (in grams).

Using the Qe data, Two isotherm models (Langmuir and Freundlich) were built. They are the most used to describe sorption specificities.

The Langmuir model is based on monolayer sorption on a homogeneous surface, using the equation (2) (Ho et al., 2005).

$$(2)\ \mathrm{Qe} = \frac{QmKaCe}{1 + \mathrm{KaCe}}$$

With Ce, the Pb concentration at equilibrium (mg.L^{-1}), Qe the quantity of Pb sorbed (mg.g^{-1}), Qm the sorption capacity (constant), and Ka the adsorption constant.

The Qm and Ka constants were determined by plotting Ce/Qe vs. Ce, which had a straight line with a slope of 1/Qm and an intercept of 1/KaCe.

The Freundlich model is based on multilayer sorption on a heterogeneous surface, using equation (3) (Ho et al., 2005).

$$(3)\ Qe = KfCe^{1/n}$$

With Qe the quantity of Pb sorbed ($mg.g^{-1}$), Ce the Pb concentration at equilibrium ($mg.L^{-1}$), Kf the sorption capacity constant and 1/n the sorption density constant.

The Kf and 1/n constants were determined by plotting LogQe *vs*. LogCe, which gives a straight line with a slope of 1/n and an intercept of LogKf.

6. Statistical analysis

Data were analyzed using R software version 3.6.1 (Team, 2000). Means were compared using the ANOVA test, followed by a Tukey post-hoc test. For the first experiment, a comparison was made inside each amendment type. The time effect was also evaluated on the SPW data. For the second experiment, all treatments were compared using the same procedure described above. In addition, the data of SPW at T0 and TF were compared by a Student test. The difference was considered significant at $p < 0.05$.

Results

1. First phytotoxicity test: single amendment.

a. Soil pore water pH.

At the beginning of the experiment (T0), SPW pH of the non-amended Pontgibaud technosol was acidic (pH 4.7) (Figure 1). Among the biochars, only four, *i.e*. HW3, BS1, BS2, and BA, increased SPW pH compared to PG, by 1.2-, 1.5-, 0.9- and 1.6-units, respectively. In the treatments enriched by activated carbon, ACN1, EK5, L5K, LC, and M630 addition increased SPW pH by 1.1, 1.6, 0.9, 1.5, and 1.1 units, respectively, compared to PG. The highest increase was observed with EK5. On the contrary, the activated carbon L27 induced a 2.2 unit decrease in SPW pH. Finally, all the redmuds increased SPW pH at similar levels, around 1.7 units.

After 14 days, SPW pH of PG was still acidic (pH 4.4) and all the biochars except PB2 increased SPW pH, the highest increase was measured with BA (2.5 units). Similarly, except L27, which induced a 1.2-units decrease in SPW pH, all the activated carbons increased SPW pH compared to PG. All the redmuds increased SPW pH at a similar level, around 2 units.

At the end of the experiment (T29), the SPW pH of PG was 4.5. Except for the biochars HW4 and PB2, which had no effect, all the biochars increased SPW pH compared to PG, between 1.1 and 2.4 units. The highest increase was found with the BA biochar. The activated carbon L27 induced a 1-unit decrease in SPW pH while all the other activated carbons increased it, by 0.8 to 1.9 units, compared to PG. Finally, all the redmuds led to a 1.7- to 2-units rise in SPW pH.

In addition, the evolution of pH with time was assessed. The SPW pH of PG did not evolve during the experiment time course (Table S2). For the biochar-amended conditions, in all the cases except PHW4 and PBM, SPW pH increased between T0 and T14, by 0.7 units on average. In the activated carbon amended conditions, different trends were observed. For PACN1 and PL5K, SPW pH increased between T14 and T29, by 0.4 units, while for PACN2, PLC, and PM2K, it increased between T0 and T14, by 0.8, 0.3, and 0.7 units, respectively. For PL27, SPW pH increased by 1 unit between T0 and T29 while no evolution in SPW pH was observed in the case of PEK5 and PM630. Finally, SPW pH increased with time in the redmud amended treatments.

b. Soil pore water electrical conductivity.

At T0, the EC of the SPW of non-amended PG was 295 µS.cm^{-1} (Figure S1). Only the biochars BA and CN increased SPW EC compared to PG, SPW EC was higher for PBA (702 µS.cm^{-1}) than PCN (474 µS.cm^{-1}). Three activated carbons increased SPW EC compared to PG, L27 (3.7-fold increase), EK5 (2.3-fold increase), and LC (2.3-fold rise), the highest increase was measured with L27. All the redmuds increased SPW EC, RMM induced a higher increase, 5.1-fold, than RMC and RMB, which increased SPW EC only by 3.3 and 3.6 times, respectively.

At T14, SPW EC of PG was 538 µS.cm^{-1} and only the addition of the BS1, BS2 and, BA biochars increased SPW EC compared to PG, by 1.7-, 1.7- and 3.1-fold, respectively. The highest increase was found with the addition of BA. Two activated carbons, EK5 and LC, increased SPW EC, by 1.8-fold, whereas one, L5K, decreased it by 30 % compared to PG. Finally, the redmuds RMC and RMM tripled SPW EC.

At T29, the SPW EC was only affected by one biochar, one activated carbon, and two redmuds. In more detail, the biochar BA induced a 2.3-times rise in SPW EC while the other biochars had no effect. Among the activated carbons, only EK5 increased SPW EC compared to PG, by 1.7-fold, while among the redmuds, RMC and RMM doubled SPW EC.

When looking at the evolution of SPW EC with time, different trends were observed. The SPW increased between T0 and T14 for the treatments PHW3, PHW4, PBS1, PBS2, PPB1, PPB2, PPB3, PBA, PBM, PEK5 and PLC (Table S2). It increased between T0 and T29 for PACN1, PACN2, PL5K, PM2K, and PM630 whereas it decreased between T0 and T14 in the treatment PL27.

c. Soil pore water Pb concentrations.

At T0, SPW Pb concentration in the PG treatment was high, around 11 mg.L^{-1} (Figure 2). In the biochar treatments, only the addition of BA decreased, by 64 %, SPW Pb concentration compared to PG. When adding activated carbons, ACN1, EK5 and LC decreased SPW Pb concentration, by 57 %, 78 %, and 72 %, respectively, compared to PG, whereas L27 increased it. Finally, all the redmuds decreased SPW Pb concentration compared to PG, the most efficient redmud to decrease Pb mobility was RMM, which induced a 78 % decrease in SPW Pb concentration.

At T14, SPW Pb concentration was 7.7 mg.L^{-1} in PG technosol and all the biochar amendments decreased SPW Pb concentration, between 27 and 80 %, except HW4 and PB2. The highest decrease was measured with BA. The three activated carbons ACN1, EK5, and LC decreased SPW Pb concentration, by 42 %, 49 %, and 61 %, respectively. All the redmuds reduced Pb mobility at similar levels (around 60 %).

At T29, the Pb concentration measured in the non-amended PG was around 7 $mg.L^{-1}$ (Figure 2). The biochar BA induced the highest decrease in SPW Pb concentration (72 %) while the biochars BS1 and BS2 led to a lower decrease, 63 %, and 40 %, respectively. The activated carbons L5K and M2K increased SPW Pb concentration by 1.6- and 1-7-fold, respectively, compared to PG. Finally, all three redmuds decreased SPW Pb concentration at a similar level, *i.e.* around 25 %.

The analysis of the evolution of SPW pH concentrations showed that it increased between T14 and T29 in several treatments, *i.e.* PHW3, PHW4, PPB1, PPB3, PCN, PBM, PACN1, PACN2, PEK5, PL5K, PLC, PM2K, PM630, PRMC, and PRMM; while no evolution was observed in the other treatments (Table S2).

d. Soil pore water As concentrations.

At T0, SPW As concentration was low in PG, less than 0.1 $mg.L^{-1}$ and biochar addition had no effect, whatever the biochar used (Figure S2). Similarly, activated carbons had no effect, except L27, which greatly increased SPW As concentration, by 271 times, compared to PG. On the contrary, all the redmuds decreased SPW As concentrations at similar levels (around 40 %).

At T14, SPW As concentration of the PG treatment was almost 0.1 $mg.L^{-1}$. All the biochars decreased SPW As concentrations compared to PG, by 30 to 60 % on average, the highest decrease was measured with BS2 (59 %) and PB1 (60 %). Similar to T0, activated carbons had no effect except for L27, which induced a great mobilization of As, by increasing SPW As concentration by 151 times compared to PG. All the redmuds decreased SPW As concentration, around 45-50 %, with no significant difference between the three redmuds.

At T29, As concentration of the PG SPW was 0.07 $mg.L^{-1}$. An increase in SPW As concentration was measured with the addition of the biochars HW3 (1.8-fold), HW4 (2.2-fold), CN (2.3-fold), and BM (2.5-fold), and the activated carbon L27 (174-fold), whereas redmud amendments had no effect.

When looking at the evolution of the SPW As concentration with time, a decrease was observed between T0 and T14 in the case of PHW4, PPB1, PPB2, PPB3, and PL27, while an increase was observed for PG, PHW3, PBS1, and PBA (Table S2). In the case of PBS2, PBM, and PRMB, SPW As concentration first decreased from T0 to T14, then increased between T14 and T29. The SPW As concentration increased between T14 and T29 in the treatments PACN1, PACN2, PL5K, PM2K, PM630, PRMC, and PRMM, while in the treatment PEK5, the increase was observed between T0 and T29 (Table S2).

e. *Phaseolus vulgaris* plant dry weight.

. In non-amended PG, *Phaseolus vulgaris* plants produced low biomass, with 0.08 g leaves, 0.06 g stems, and 0.15 g roots (Figure 3). The biochars HW3, BS1 and BA increased stem, leaf and root DW compared to PG, while BS2 only increased the DW of the aerial parts (leaves and stems) (Figure 3). In more detail, leaf DW was increased by 2.5-, 3- and 3.9-fold following the addition of HW3, BS1 and BA, respectively, the stem DW by 2.3-, 2.7- and 3.5-fold, respectively, and the root DW by 2.3-, 2.7- and 3.1-fold respectively. The biochar BS2 led to a 2.3 and 2 times increase in leaf and stem DW compared to PG, respectively.

Based on the results of this phytotoxicity test, it can be stated that not all amendments affected SPW physicochemical properties, metal(loid) mobility, and plant growth. Therefore, five amendments were selected for further tests: two biochars, BS2 and BA, two activated carbons, EK5 and L27, and one redmud, RMM. The two biochars were the ones having the best benefits on SPW pH, [Pb] and plant growth among all the biochars; EK5 was the only activated carbon inducing an increase in SPW pH, EC, a decrease in SPW [Pb], and an improvement of plant growth while L27 induced the best plant growth. Finally, among the three redmuds, RMM was the only one improving all soil pore water and plant parameters.

2. Second phytotoxicity test: combined amendments.

a. Soil pore water parameters.

At T0, SPW pH of PG was acidic (pH 4.7) and increased with the application of RBA (+2.2 units), RBS2 (+1.9 units) and REK5 (+1.9 units) (Table 2). At TF, the acidic pH of Pontgibaud technosol (pH 4.1) was increased by all the tested amendment combinations, between 2.3 and 2.8 units. An increase in SPW pH between T0 and TF was measured in the RL27 treatment while a decrease was found for REK5.

At T0, SPW EC of PG was 295 µS.cm^{-1} and all the combinations of amendments increased it, between 3.4 and 5.7-fold (Table 2). The highest increases were measured in RBA and REK5. Similarly, at TF, SPW EC was 507 µS.cm^{-1} and all the combined amendments increased it. In detail, increase rates were 7.8-fold, 7.5-fold, 7.9-fold, and 6.7-fold with RBA, RBS2, RL27, and REK5, respectively. This time, no difference between combined amended treatments was observed. In all cases, SPW EC increased between T0 and TF.

The SPW As concentration was 0.07 mg.L^{-1} in PG at T0, this concentration increased with the application of REK5 (4.3-fold) and RL27 (79-fold) (Table 2). At TF, combined amendment treatments did not affect SPW As concentrations. Between T0 and TF, SPW As concentration increased in PG and decreased in the four combined treatments (RBA, RBS2, RL27, and REK5).

At T0, SPW Pb concentration was high in PG (10.8 mg.L^{-1}) and all the combined amendments reduced Pb mobility by 80 % (RBA), 67 % (RBS2), 82 % (RL27), and 58 % (REK5), the best-combined amendment being RL27. Similarly, at TF, SPW Pb concentration of PG was 14.9 mg.L^{-1} and the amendments decreased it, between 80 % and 87 %, the highest decrease was measured again with RL27. Between T0 and TF, SPW Pb concentration increased in the PG treatment and decreased in the RL27 treatment.

b. *Phaseolus vulgaris* dry weight production

On PG, the plants of *Phaseolus vulgaris* produced 0.05 g of leaves 0.07 g of stems, and 0.04 g of roots after 15 days of growth (Figure 4). All the amendments increased stem, leaf, and root DW. Stem DW was increased between 2.3 and 2.8-fold at similar levels between the amended conditions, the highest leaf DW was observed with RBS2 (7.4-fold) and REK5 (6.8 fold), while RL27 induced the lowest root DW increase (2.5-fold) compared to the other three amendment combinations.

3. Sorption test

The Langmuir and Freundlich models (with experimental and theoretical values) are shown in Figure S3 and the adsorption constants were determined and are shown in Table 3.

The R^2 values of both isotherms showed that data were better explained by the Langmuir model, except for BS2 biochar, which had similar R^2 values for both models. This demonstrates that, for all amendments, sorption was based on a monolayer process on a homogeneous surface. However, the five amendments differed in their sorption capacity, as shown by their Qm values. The two activated carbons had a higher sorption capacity (Qm = 156 $mg.g^{-1}$ for EK5 and Qm = 162 $mg.g^{-1}$ for L27) than the two biochars (Qm = 92 $mg.g^{-1}$ for BA and Qm = 63 $mg.g^{-1}$ for BS2), while RMM had the highest sorption capacity (qm = 217 $mg.g^{-1}$).

Discussion

1. Carbon-based amendment effect

The soil pH was generally shown to increase following a carbon-based amendment, which is consistent with previous studies (Basalirwa et al., 2020; Dai et al., 2018; M. Lebrun et al., 2021). Such a rise in pH after biochar and activated carbon amendment was also observed in this study, except for the L27 activated carbon. Several mechanisms have been given to explain this pH increase. (1) The biochars and activated carbons generally have a high pH, which induces a liming effect when they are added to the soil, especially in the case of acidic sandy soil with low buffering capacity (Ahmad et al., 2014; Ippolito et al., 2017). This was supported by a correlation between the pH of the carbon amendment and the pH of the SPW at T0 ($R^2 = 0.74$, p-value < 0.001), T14 ($R^2 = 0.65$, p-value < 0.01) and T29 ($R^2 = 0.65$, p-value < 0.01). (2) Carbon-based amendments are characterized by high ash content, containing alkaline oxide or carbonate minerals that dissolve in the soil water (Dai et al., 2018). (3) The surface of these amendments is made of many functional groups, *e.g.* carboxyl (C(=O)OH), phenols (aromatic compounds with an OH group), carbonyls (C=O), and pyrones –C=O); these functional groups are mainly alkaline but can also bind H^+ ions and thus increase pH (Houben and Sonnet, 2015; Lebrun et al., 2018b). Moreover, one amendment, L27 activated carbon, induced acidification of the soil pore water. Two explanations can be given to such observation: (i) the L27 activated carbon was acidic and its pH was lower than the technosol's (pH 1.9), which could have induced a decrease in soil pH, especially if the soil had a low buffering capacity; (ii) the activation of this amendment was made using phosphoric acid, which can dissociate in the soil in $H_2PO_4^-$ and H^+, thus reducing soil pH (Zeng et al., 2017).

Similarly to pH, the addition of carbon-based amendments to the Pontgibaud technosol generally increased soil pore water electrical conductivity, which was consistent with previous studies (Ahmad et al., 2017; Derakhshan Nejad et al., 2021). The augmentation in soil EC has been related to the elevated EC of the amendments, and to the dissolution of salts they contained (Ahmad et al., 2017; Derakhshan Nejad et al., 2021), as supported by the correlation between amendment EC and SPW EC at T0 ($R^2 = 0.81$, p-value < 0.001), T14 ($R^2 = 0.61$, p-value < 0.01) and T29 ($R^2 = 0.61$, p-value < 0.01).

Lead concentration in the non-amended contaminated Pontgibaud soil pore water indicates its high mobility and thus potential to be leached during a rain event. It is thus of primary importance to reduce the mobility of Pb. Previous researches demonstrated the efficiency of biochar and activated carbon in immobilizing of Pb (Derakhshan Nejad et al., 2021; He et al., 2019; Lebrun et al., 2017). Three main mechanisms can be related to the Pb immobilization with biochar and activated carbon. Firstly, as demonstrated before, the carbon-based amendments increased soil pH, which is known to reduce cation metal mobility (Álvarez et al., 2020; Kumpiene et al., 2019; Puga et al., 2015), as it favors their precipitation and hydrolysis (Derakhshan Nejad et al., 2021; Kumpiene et al., 2019). The increase in soil pH is often one of the first explanations given for the cation immobilization. However, this study showed that the amendments inducing the highest soil pore water pH rise were not systematically the most efficient for Pb immobilization. This was particularly observed for the later sampling time, indeed correlation between SPW pH and SPW Pb concentrations were significant at T0 ($R^2 = -0.92$, p-value < 0.001) and T14 ($R^2 = -0.70$, p-value < 0.01), but not for the last sampling date, T29. Thus, pH rise cannot be the only and main explanation in the present case and other mechanisms must have acted. The second mechanism of Pb immobilization can be its interaction with the functional groups present at the surface of the amendments (Lebrun et al., 2018b). Concerning the second mechanism given, Pb can be sorbed on the amendment surface by forming precipitates with elements on the surface, such as $PbCO_3$ and organic matter (M Lebrun et al., 2021). Moreover, correlation analyses showed that Pb immobilization was highly dependent to with the pH of the C amendment ($R^2 = 0.81$, p-value < 0.001), and moderately to the specific surface area of the C amendment ($R^2 = 0.62$, p-value < 0.01), as well as its carbon content ($R^2 = 0.51$, p-value < 0.05) and H content ($R^2 = -0.59$, p-value < 0.05).

Globally, the carbon-based amendments used in this study did not affect SPW As concentrations, or only slightly, except for the great mobilization induced by the activated carbon L27. Such reduced effect of biochar and activated carbon on As mobility has also been observed in the studies of Lebrun et al., (2017) and Hartley et al., (2009) and can be explained by the fact that both As and the amendment surface are negatively charged and thus repulsion occurs, preventing As sorption on biochar (Lebrun et al., 2018b). However, a brief immobilization of As occurs with the biochar amendments after 14 days, which could be related to a modification of the biochar surface once in the soil and thus a capacity to sorb As (M Lebrun et al., 2021; Tabassum et al., 2019). these benefit were only short-term because it was not observed after 29 days. On the contrary, L27 mobilized As, which could be due to the phosphorus present in the activated carbon (results of its activation with phosphoric acid). The As and P ions are chemically similar and thus compete for the same sorption sites; thus the addition of P into the soil through L27 could have displaced As from soil sorption sites, leading to its liberation in the soil pore water (Hartley et al., 2009; Khalid et al., 2017). However, it has to be noted that As mobility was low compared to the one of Pb, with concentration below the limit value for irrigation water of 0.1 $mg.L^{-1}$ (Ashraf et al., 2019), and that although it was not assessed, it can be assumed that the substrate had oxidic conditions, and thus As will be mainly found in the form of As(V) (Trakal et al., 2017), which is less toxic than As(III). Compared to lead, arsenic will pose a lower risk than Pb, except in presence of L27, in which As pore water concentration rose above limit value. Finally, when evaluating the effect of biochar properties on As immobilization, the correlation analyses showed that As immobilization was influenced by the carbon-amendment pH ($R^2 = -0.74$, p-value < 0.001) and moderately by the amendment's EC ($R^2 = 0.60$, p-value < 0.01), specific surface area ($R^2 = 0.50$, p-value < 0.05) and total pore volume ($R^2 = 0.63$, p-value < 0.01).

The technosol of Pontgibaud was characterized by an acidic pH and elevated SPW As and Pb concentrations, which can make the soil too toxic for plant growth. Such toxicity was attested by the low dry weight production of *Phaseolus vulgaris* plants on non-amended technosol. To reduce soil toxicity and thus ameliorate plant growth, many studies used biochar and activated carbon (Břendová et al., 2016; Lebrun et al., 2018a; Nie et al., 2018). Several of the biochars and activated carbons used here induced an amelioration of *Phaseolus vulgaris* dry weight, which testified of their ability to reduce soil toxicity. The amelioration of plant growth can be related to the improvement of the soil conditions, *i.e.* reduction of soil acidity and Pb immobilization, but also the supply of nutrients by the amendments (Břendová et al., 2016; Nie et al., 2018). Moreover, leaf, stem and root dry weights were moderately correlated with amendment EC, with R^2 values of 0.66 (p-value < 0.01) for leaves, 0.51 (p-value < 0.05) for stems and 0.62 (p-value < 0.01) for roots.

Globally, this study using several biochars and activated carbons demonstrated the efficiency of carbon-based amendments in reducing soil acidity and immobilizing Pb. However, not all amendments had beneficial effects on these two parameters, and thus plant growth. Some only affected soil pH and Pb behavior after 14 or 29 days. This demonstrates that the beneficial effects of carbon-based amendments are dependent on the amendment properties. Correlation analyses showed that the main properties of the carbon-based amendments affecting soil properties were pH, EC, and to a lesser extent specific surface area, total pore volume, and carbon and hydrogen content, while the property influencing plant growth was amendment EC. More precisely, As and Pb were better immobilized with carbon amendments having a higher pH, Pb was also better immobilized by amendments with high hydrogen content while As immobilization was more successful with amendments harboring lower EC, carbon content, surface-specific area, and total pore volume. Moreover, based on the results of different time sampling, it seems that some amendments need more time than others to be efficient, and thus their aging in the soil will probably modify their properties, leading to positive outcomes on soil and metal(loid)s (Lebrun et al., 2018a).

2. Redmud amendment effect

Globally, all three redmuds had the same effects on the soil, the metal(loid)s and the bio-indicator plant; and no difference was found between the three redmuds in most cases. More precisely, redmud application to the acidic technosol of Pontgibaud led to an increase in soil pore water pH and EC, an immobilization of As and Pb, as demonstrated with the decrease in SPW As and Pb concentrations, and an improvement of plant growth. Such results have been previously observed (Feigl et al., 2012; Lee et al., 2014; Thouin et al., 2019). Finally, it can be noted that redmuds were generally more efficient in immobilizing metal(loid)s than the carbon-based amendments.

Redmud is generated during the bauxite production through the Bayer process, which makes redmud highly alkaline (Zhou et al., 2017). This alkaline pH, between 8 and 12 in this study, induced the observed rise in soil pH.

The Bayer process uses caustic soda, thus redmud has a high EC. This high content of salts is liberated in the soil solution when redmud is added to the soil and thus soil EC increases (Gautam and Agrawal, 2017). Such mechanism could be responsible for the results observed here, which are consistent with previous studies (Gautam and Agrawal, 2017; Lee et al., 2014).

Similarly to carbon-based amendments, redmud has been shown to effectively immobilize cation metals, such as Pb. However, they were also demonstrated to be efficient towards As, contrary to carbon-based amendments. Indeed, precipitated Al, Fe, and Mn minerals, which are contained in redmud, are very suitable to sorb M^{2+} cations, such as Pb^{2+}, as well as oxyanions, such as AsO_4^- (Feigl et al., 2012; Thouin et al., 2019; Zhou et al., 2017). Two main mechanisms can explain the immobilization of As and Pb. The first mechanism is the pH increase induced by the redmud amendment (Feigl et al., 2012; Thouin et al., 2019). Indeed, cation elements tend to precipitate and be immobilized when pH increases. However, such a mechanism only explains Pb immobilization, since Pb is a cation while As is an anion and thus will tend to be mobilized with the rise in soil pH. The second mechanism can explain both As and Pb immobilization: redmud contains adsorption sites, such as Fe and Al oxides, as well as hydroxyl groups on its surface, and thus arsenic and lead can be sorbed on the redmud surface (Feigl et al., 2012; Zhou et al., 2017).

Finally, the amelioration of plant growth, relating to the reduction of soil toxicity with the redmud amendments, has been previously observed in phytotoxicity tests, using different plants than *Phaseolus vulgaris* (Feigl et al., 2012; Thouin et al., 2019). As shown in the previous section, redmud amendment reduced soil acidity and immobilized As and Pb, which can explain the amelioration of *Phaseolus vulgaris* growth (Feigl et al., 2012).

3. Sorption capacity

The results of the sorption test realized were used to build sorption isotherm models. Between the two models, the Langmuir model, based on monolayer sorption on a homogenous surface, better fitted the data compared to the Freundlich model. All the Ka values of the Langmuir model were positive, which demonstrated that Pb sorption on the five amendments (BS2, BA, L27, EK5, and RMM) was favorable (Arcibar-Orozco et al., 2014). Moreover, Qm values showed that activated carbons, which had higher surface areas, had a higher sorption capacity than the biochars, characterized by a lower surface area. The positive relation between the amendment surface area and the sorption capacity was in contradiction with the studies of Agrafioti et al., (2014) and Cao et al., (2009), who observed an opposite trend. Therefore, from this study, it can be concluded that the surface area could affect Pb sorption on the carbon-based amendments, even indirectly. Indeed, a higher surface area could mean a higher number of carboxylic and phenolic groups on the material surface, which can interact with Pb^{2+} through chelate formation, ion exchange, or co-precipitation, forming $PbCO_3$ or $Pb(HCO_3)_2$ for instance (Trakal et al., 2014).

This possible mechanism is supported by the shape of the sorption isotherms. Indeed, at low Pb concentrations, Pb sorption capacity increased to reach a plateau at higher Pb concentrations. Such a trend can be the result of surface precipitation processes (Inyang et al., 2012). In more detail, amendments, especially carbon-based ones, release negatively charged ions into the solution, such as carbonates and phosphates. These elements can precipitate Pb, and can completely remove Pb when Pb is at a low concentration. However, at higher Pb concentrations, negatively charged ions are all consumed by Pb and no more precipitation can occur and thus sorption reached a plateau. Such a precipitation process on phosphates could explain the higher sorption capacity of the L27 activated carbon, which has been activated using phosphoric acid and could have thus liberated more phosphate to the solution, and thus more Pb was precipitated. Indeed, as demonstrated in the study of Netherway et al., (2019), in presence of phosphorus-rich biochars, Pb was immobilized through the precipitation between Pb and phosphorus, liberated even under acidic pH, as well as the formation of pyromorphite.

Moreover, this sorption mechanism was confirmed by the observation of the pH of the solution before and after the sorption (Table S3). At the initial low Pb concentration, the pH after the sorption was higher than the one before the sorption. At this Pb concentration, there are still carbonates and phosphates in the solution, not precipitated with Pb, and thus they increase the pH of the solution. However, at a higher initial Pb concentration, the final pH was about the same as the initial pH, or only slightly higher, meaning that this time, all carbonated and phosphates were consumed by Pb, and thus the remaining Pb in the solution could induce an acidification (Inyang et al., 2012).

Based on the sorption test, it can be assumed that the combination of redmud with activated carbon will lead to a higher Pb immobilization than the combination of redmud and biochar.

4. The benefits of amendment combination

Following the first phytotoxicity test, aiming at evaluating several biochars, activated carbons, and redmuds, and selecting five of them based on their effects on the soil, metal(loid) immobilization, and plant dry weight, a second phytotoxicity test was performed. This second test used the five selected amendments in combination. More precisely, the redmud, which is very effective for As, contrary to carbon-based amendments, was applied in combination with either biochar or activated carbon. Such a combination has been studied only a few times (Lebrun et al., 2020; Lebrun et al., 2021b; Simiele et al., 2020).

The results of the amendment combination showed an increase in soil pore water pH following amendments, except for the combination RL27 at the beginning of the experiment, following other published works (Fresno et al., 2018; Manhattan Lebrun et al., 2021a).. As explained with the single amendment, the properties of the amendments, such as pH, surface functional groups and ash content, can explain such a pH rise. The decrease in soil pH with RL27 can be explained by the acidic pH of L27. Moreover, when comparing the pH change in the single and combined phytotoxicity test, the pH increase was higher with the combination compared to the individual amendments. Especially, although SPW pH decreased at T0 with RL27, this decrease was lower than when L27 was applied alone, demonstrating that redmud could counterbalance the acidity of L27, leading to lower acidification at T0 and even to an increase in soil pH towards the end of the experiment.

Contrary to pH, all the amendments increased soil pore water EC, which can be related to their high EC and salt contents. Moreover, in all the cases, SPW EC was higher in the combination treatments than the single amendments. This was expected since more amendments were added in total (3 % vs. 1 % or 2 %) and thus led to more salts added.

At the beginning of the experiment, an increase in SPW As concentration was observed in two treatments, which disappeared at the end of the experiment. The combination of amendments in this study showed only small effects on As mobility. However, the increase in SPW As concentration with RL27 was expected, since L27 is an activated carbon containing phosphoric acid, and whose phosphate can compete with As for sorption sites, as observed for the L27 single amendment. However, when comparing the single L27 amendment with the RL27 combination, the As mobilization was lower with the combination. It can thus be hypothesized that the As released by the competition between P contained in L27 and As could have been sorbed on redmud surface.

All the amendment treatments reduced SPW Pb concentrations, similarly to the studies of Lebrun et al., (2020) and Simiele et al., (2020). Such efficiency in Pb immobilization was already demonstrated in the single amendment test and could have occurred through the sorption of Pb on the amendment surface, such as shown in the sorption tests. Activated carbons had a higher sorption capacity than biochar, and thus their combination with redmud was expected to induce a better Pb immobilization. However, the higher immobilization was found with RL27, while the other activated carbon EK5 (treatment REK5) induced the lowest Pb immobilization, indicating that other reactions than sorption also occurred, i.e.,. pH increase, and precipitation of minerals containing carbonates or phosphates. When comparing single amendments and combinations, the amendments were more efficient when applied in combination, which could be due to the higher pH increase induced as well as the presence of more sorption sites for Pb, due to more amendment.

Following the amelioration of the soil conditions, and similarly to what was observed in the single amendment test, plant dry weight increased. When comparing both phytotoxicity tests, the same increase was measured with the single and combined amendments, although more amendments were added in total, except for RBA and RBS2, which tended to induce higher DW than the single BA, BS2, and RBM treatments.

Conclusion

This study demonstrated that biochar, activated carbon and redmud were efficient amendments to ameliorate the properties of contaminated soil, i.e.,. buffering effect, immobilization of pollutants, and reduction of soil phytotoxicity. Moreover, it also showed that for biochar and activated carbon, effects depended on the feedstock and particle size, and were linked to amendment properties such as pH, electrical conductivity, surface area, and total pore volume. Finally, the combination of redmud with biochar was more efficient to lower soil phytotoxicity than their single application. Therefore, we suggest using redmud and biochar for the remediation of multi-contaminated soil. We also suggest performing more studies with this combination on other sites, polluted by different metal(loid)s than As and Pb. Finally, we suggest to prepare and test an Al-oxide-biochar composite, which will have the benefits of both biochar and redmud, to remediate multi-contaminated soils.

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References

Agrafioti, E., Kalderis, D., Diamadopoulos, E., 2014. Arsenic and chromium removal from water using biochars derived from rice husk, organic solid wastes and sewage sludge. J. Environ. Manage. 133, 309–314. https://doi.org/10.1016/j.jenvman.2013.12.007

Ahmad, M., Lee, S.S., Lee, S.E., Al-Wabel, M.I., Tsang, D.C.W., Ok, Y.S., 2017. Biochar-induced changes in soil properties affected immobilization/mobilization of metals/metalloids in contaminated soils. J. Soils Sediments 17, 717–730. https://doi.org/10.1007/s11368-015-1339-4

Ahmad, M., Lee, S.S., Lim, J.E., Lee, S.-E., Cho, J.S., Moon, D.H., Hashimoto, Y., Ok, Y.S., 2014. Speciation and phytoavailability of lead and antimony in a small arms range soil amended with mussel shell, cow bone and biochar: EXAFS spectroscopy and chemical extractions. Chemosphere 95, 433–441. https://doi.org/10.1016/j.chemosphere.2013.09.077

Álvarez, M.L., Méndez, A., Paz-Ferreiro, J., Gascó, G., 2020. Effects of Manure Waste Biochars in Mining Soils. Appl. Sci. 10, 3393. https://doi.org/10.3390/app10103393

Arcibar-Orozco, J.A., Josue, D.-B., Rios-Hurtado, J.C., Rangel-Mendez, J.R., 2014. Influence of iron content, surface area and charge distribution in the arsenic removal by activated carbons. Chem. Eng. J. 249, 201–209. https://doi.org/10.1016/j.cej.2014.03.096

Ashraf, Sana, Ali, Q., Zahir, Z.A., Ashraf, Sobia, Asghar, H.N., 2019. Phytoremediation: Environmentally sustainable way for reclamation of heavy metal polluted soils. Ecotoxicol. Environ. Saf. 174, 714–727. https://doi.org/10.1016/j.ecoenv.2019.02.068

Basalirwa, D., Sudo, S., Wacal, C., Namirembe, C., Sasagawa, D., Yamamoto, S., Masunaga, T., Nishihara, E., 2020. Effect of activated carbon on greenhouse gas emissions, seed yield, soil chemical properties and isoflavone content of soybean genotypes with varying nodulation capacities under sandy soil conditions. Rhizosphere 14, 100202. https://doi.org/10.1016/j.rhisph.2020.100202

Bertocchi, A.F., Ghiani, M., Peretti, R., Zucca, A., 2006. Red mud and fly ash for remediation of mine sites contaminated with As, Cd, Cu, Pb and Zn. J. Hazard. Mater. 134, 112–119. https://doi.org/10.1016/j.jhazmat.2005.10.043

Břendová, K., Zemanová, V., Pavlíková, D., Tlustoš, P., 2016. Utilization of biochar and activated carbon to reduce Cd, Pb and Zn phytoavailability and phytotoxicity for plants. J. Environ. Manage. 181, 637–645. https://doi.org/10.1016/j.jenvman.2016.06.042

Briffa, J., Sinagra, E., Blundell, R., 2020. Heavy metal pollution in the environment and their toxicological effects on humans. Heliyon 6, e04691. https://doi.org/10.1016/j.heliyon.2020.e04691

Burges, A., Alkorta, I., Epelde, L., Garbisu, C., 2018. From phytoremediation of soil contaminants to phytomanagement of ecosystem services in metal contaminated sites. Int. J. Phytoremediation 20, 384–397. https://doi.org/10.1080/15226514.2017.1365340

Cao, X., Ma, L., Gao, B., Harris, W., 2009. Dairy-Manure Derived Biochar Effectively Sorbs Lead and Atrazine. Environ. Sci. Technol. 43, 3285–3291. https://doi.org/10.1021/es803092k

Cárdenas-Aguiar, E., Suárez, G., Paz-Ferreiro, J., Askeland, M.P.J., Méndez, A., Gascó, G., 2020. Remediation of mining soils by combining Brassica napus growth and amendment with chars from manure waste. Chemosphere 261, 127798. https://doi.org/10.1016/j.chemosphere.2020.127798

Dai, S., Li, H., Yang, Z., Dai, M., Dong, X., Ge, X., Sun, M., Shi, L., 2018. Effects of biochar amendments on speciation and bioavailability of heavy metals in coal-mine-contaminated soil. Hum. Ecol. Risk Assess. Int. J. 24, 1887–1900. https://doi.org/10.1080/10807039.2018.1429250

Derakhshan Nejad, Z., Rezania, S., Jung, M.C., Al-Ghamdi, A.A., Mustafa, A.E.-Z.M.A., Elshikh, M.S., 2021. Effects of fine fractions of soil organic, semi-organic, and inorganic amendments on the mitigation of heavy metal(loid)s leaching and bioavailability in a post-mining area. Chemosphere 271, 129538. https://doi.org/10.1016/j.chemosphere.2021.129538

Egene, C.E., Van Poucke, R., Ok, Y.S., Meers, E., Tack, F.M.G., 2018. Impact of organic amendments (biochar, compost and peat) on Cd and Zn mobility and solubility in contaminated soil of the Campine region after three years. Sci. Total Environ. 626, 195–202. https://doi.org/10.1016/j.scitotenv.2018.01.054

Feigl, V., Anton, A., Uzigner, N., Gruiz, K., 2012. Red Mud as a Chemical Stabilizer for Soil Contaminated with Toxic Metals. Water. Air. Soil Pollut. 223, 1237–1247. https://doi.org/10.1007/s11270-011-0940-4

Fresno, T., Moreno-Jiménez, E., Zornoza, P., Peñalosa, J.M., 2018. Aided phytostabilisation of As- and Cu-contaminated soils using white lupin and combined iron and organic amendments. J. Environ. Manage. 205, 142–150. https://doi.org/10.1016/j.jenvman.2017.09.069

Gascó, G., Álvarez, M.L., Paz-Ferreiro, J., Méndez, A., 2019. Combining phytoextraction by Brassica napus and biochar amendment for the remediation of a mining soil in Riotinto (Spain). Chemosphere 231, 562–570. https://doi.org/10.1016/j.chemosphere.2019.05.168

Gautam, M., Agrawal, M., 2017. Phytoremediation of metals using vetiver (Chrysopogon zizanioides (L.) Roberty) grown under different levels of red mud in sludge amended soil. J. Geochem. Explor. 182, 218–227. https://doi.org/10.1016/j.gexplo.2017.03.003

Ghosh, D., Maiti, S.K., 2020. Biochar assisted phytoremediation and biomass disposal in heavy metal contaminated mine soils: a review. Int. J. Phytoremediation 1–18. https://doi.org/10.1080/15226514.2020.1840510

Guo, M., Song, W., Tian, J., 2020. Biochar-Facilitated Soil Remediation: Mechanisms and Efficacy Variations. Front. Environ. Sci. 8, 521512. https://doi.org/10.3389/fenvs.2020.521512

Hartley, W., Dickinson, N.M., Riby, P., Lepp, N.W., 2009. Arsenic mobility in brownfield soils amended with green waste compost or biochar and planted with Miscanthus. Environ. Pollut. 157, 2654–2662. https://doi.org/10.1016/j.envpol.2009.05.011

He, L., Zhong, H., Liu, G., Dai, Z., Brookes, P.C., Xu, J., 2019. Remediation of heavy metal contaminated soils by biochar: Mechanisms, potential risks and applications in China. Environ. Pollut. 252, 846–855. https://doi.org/10.1016/j.envpol.2019.05.151

Ho, Y.-S., Chiu, W.-T., Wang, C.-C., 2005. Regression analysis for the sorption isotherms of basic dyes on sugarcane dust. Bioresour. Technol. 96, 1285–1291. https://doi.org/10.1016/j.biortech.2004.10.021

Houben, D., Sonnet, P., 2015. Impact of biochar and root-induced changes on metal dynamics in the rhizosphere of Agrostis capillaris and Lupinus albus. Chemosphere 139, 644–651. https://doi.org/10.1016/j.chemosphere.2014.12.036

Hua, Y., Heal, K.V., Friesl-Hanl, W., 2017. The use of red mud as an immobiliser for metal/metalloid-contaminated soil: A review. J. Hazard. Mater. 325, 17–30. https://doi.org/10.1016/j.jhazmat.2016.11.073

Inyang, M., Gao, B., Yao, Y., Xue, Y., Zimmerman, A.R., Pullammanappallil, P., Cao, X., 2012. Removal of heavy metals from aqueous solution by biochars derived from anaerobically digested biomass. Bioresour. Technol. 110, 50–56. https://doi.org/10.1016/j.biortech.2012.01.072

Ippolito, J.A., Berry, C.M., Strawn, D.G., Novak, J.M., Levine, J., Harley, A., 2017. Biochars Reduce Mine Land Soil Bioavailable Metals. J. Environ. Qual. 46, 411–419. https://doi.org/10.2134/jeq2016.10.0388

Karaca, O., Cameselle, C., Reddy, K.R., 2018. Mine tailing disposal sites: contamination problems, remedial options and phytocaps for sustainable remediation. Rev. Environ. Sci. Biotechnol. 17, 205–228. https://doi.org/10.1007/s11157-017-9453-y

Khairul, M.A., Zanganeh, J., Moghtaderi, B., 2019. The composition, recycling and utilisation of Bayer red mud. Resour. Conserv. Recycl. 141, 483–498. https://doi.org/10.1016/j.resconrec.2018.11.006

Khalid, S., Shahid, M., Niazi, N.K., Murtaza, B., Bibi, I., Dumat, C., 2017. A comparison of technologies for remediation of heavy metal contaminated soils. J. Geochem. Explor. 182, 247–268. https://doi.org/10.1016/j.gexplo.2016.11.021

Kopittke, P.M., Menzies, N.W., Wang, P., McKenna, B.A., Lombi, E., 2019. Soil and the intensification of agriculture for global food security. Environ. Int. 132, 105078. https://doi.org/10.1016/j.envint.2019.105078

Kumpiene, J., Antelo, J., Brännvall, E., Carabante, I., Ek, K., Komárek, M., Söderberg, C., Wårell, L., 2019. In situ chemical stabilization of trace element-contaminated soil – Field demonstrations and barriers to transition from laboratory to the field – A review. Appl. Geochem. 100, 335–351. https://doi.org/10.1016/j.apgeochem.2018.12.003

Kumpiene, J., Giagnoni, L., Marschner, B., Denys, S., Mench, M., Adriaensen, K., Vangronsveld, J., Puschenreiter, M., Renella, G., 2017. Assessment of Methods for Determining Bioavailability of Trace Elements in Soils: A Review. Pedosphere 27, 389–406. https://doi.org/10.1016/S1002-0160(17)60337-0

Lebrun, Manhattan, Bourgerie, S., Morabito, D., 2021a. Effects of Different Biochars, Activated Carbons and Redmuds on the Growth of Trifolium repens and As and Pb Stabilization in a Former Mine Technosol. Bull. Environ. Contam. Toxicol. https://doi.org/10.1007/s00128-021-03271-y

Lebrun, M., Macri, C., Miard, F., Hattab-Hambli, N., Motelica-Heino, M., Morabito, D., Bourgerie, S., 2017. Effect of biochar amendments on As and Pb mobility and phytoavailability in contaminated mine technosols phytoremediated by Salix. J. Geochem. Explor. 182, 149–156. https://doi.org/10.1016/j.gexplo.2016.11.016

Lebrun, Manhattan, Miard, F., Bucci, A., Fougère, L., Nandillon, R., Naclerio, G., Scippa, G.S., Destandau, E., Morabito, D., Bourgerie, S., 2021b. The rhizosphere of Salix viminalis plants after a phytostabilization process assisted by biochar, compost, and iron grit: chemical and (micro)-biological analyses. Environ. Sci. Pollut. Res.

Lebrun, M., Miard, F., Nandillon, R., Hattab-Hambli, N., Léger, J.C., Scippa, G.S., Morabito, D., Bourgerie, S., 2021. Influence of Biochar Particle Size and Concentration on Pb and As Availability in Contaminated Mining Soil and Phytoremediation Potential of Poplar Assessed in a Mesocosm Experiment. Water. Air. Soil Pollut. 232, 3. https://doi.org/10.1007/s11270-020-04942-y

Lebrun, M., Miard, F., Nandillon, R., Hattab-Hambli, N., Scippa, G.S., Bourgerie, S., Morabito, D., 2018a. Eco-restoration of a mine technosol according to biochar particle size and dose application: study of soil physico-chemical properties and phytostabilization capacities of Salix viminalis. J. Soils Sediments 18, 2188–2202. https://doi.org/10.1007/s11368-017-1763-8

Lebrun, M., Miard, F., Nandillon, R., Scippa, G.S., Bourgerie, S., Morabito, D., 2019. Biochar effect associated with compost and iron to promote Pb and As soil stabilization and Salix viminalis L. growth. Chemosphere 222, 810–822. https://doi.org/10.1016/j.chemosphere.2019.01.188

Lebrun, M., Miard, F., Renouard, S., Nandillon, R., Scippa, G.S., Morabito, D., Bourgerie, S., 2018b. Effect of Fe-functionalized biochar on toxicity of a technosol contaminated by Pb and As: sorption and phytotoxicity tests. Environ. Sci. Pollut. Res. 25, 33678–33690. https://doi.org/10.1007/s11356-018-3247-9

Lebrun, M., Miard, F., Scippa, G.S., Hano, C., Morabito, D., Bourgerie, S., 2020. Effect of biochar and redmud amendment combinations on Salix triandra growth, metal(loid) accumulation and oxidative stress response. Ecotoxicol. Environ. Saf. 195, 110466. https://doi.org/10.1016/j.ecoenv.2020.110466

Lebrun, M, Nandillon, R., Miard, F., Bourgerie, S., Visser, R., Morabito, D., 2021. Biochar application modifies soil properties of a former mine technosol: SEM/EDS study to investigate Pb and As speciation. Biomass Convers. Biorefinery. https://doi.org/10.1007/s13399-021-01289-0

Lebrun, Manhattan, Van Poucke, R., Miard, F., Scippa, G.S., Bourgerie, S., Morabito, D., Tack, F.M.G., 2021c. Effects of carbon-based materials and redmuds on metal(loid) immobilization and growth of *Salix dasyclados* Wimm. on a former mine Technosol contaminated by arsenic and lead. Land Degrad. Dev. 32, 467–481. https://doi.org/10.1002/ldr.3726

Lee, S.-H., Ji, W., Lee, W.-S., Koo, N., Koh, I.H., Kim, M.-S., Park, J.-S., 2014. Influence of amendments and aided phytostabilization on metal availability and mobility in Pb/Zn mine tailings. J. Environ. Manage. 139, 15–21. https://doi.org/10.1016/j.jenvman.2014.02.019

Liu, Si-jia, Liu, Y., Tan, X., Zeng, G., Zhou, Y., Liu, Shao-bo, Yin, Z., Jiang, L., Li, M., Wen, J., 2018. The effect of several activated biochars on Cd immobilization and microbial community composition during in-situ remediation of heavy metal contaminated sediment. Chemosphere 208, 655–664. https://doi.org/10.1016/j.chemosphere.2018.06.023

Neina, D., 2019. The Role of Soil pH in Plant Nutrition and Soil Remediation. Appl. Environ. Soil Sci. 2019, 1–9. https://doi.org/10.1155/2019/5794869

Netherway, P., Reichman, S.M., Laidlaw, M., Scheckel, K., Pingitore, N., Gascó, G., Méndez, A., Surapaneni, A., Paz-Ferreiro, J., 2019. Phosphorus-Rich Biochars Can Transform Lead in an Urban Contaminated Soil. J. Environ. Qual. 48, 1091–1099. https://doi.org/10.2134/jeq2018.09.0324

Nie, C., Yang, X., Niazi, N.K., Xu, X., Wen, Y., Rinklebe, J., Ok, Y.S., Xu, S., Wang, H., 2018. Impact of sugarcane bagasse-derived biochar on heavy metal availability and microbial activity: A field study. Chemosphere 200, 274–282. https://doi.org/10.1016/j.chemosphere.2018.02.134

Puga, A.P., Abreu, C.A., Melo, L.C.A., Paz-Ferreiro, J., Beesley, L., 2015. Cadmium, lead, and zinc mobility and plant uptake in a mine soil amended with sugarcane straw biochar. Environ. Sci. Pollut. Res. 22, 17606–17614. https://doi.org/10.1007/s11356-015-4977-6

Simiele, M., Lebrun, M., Del Cioppo, G., Scippa, S.G., Trupiano, D., Bourgerie, S., Morabito, D., 2020. Evaluation of Different Amendment Combinations Associated with Trifolium repens to Stabilize Pb and As in a Mine-Contaminated Soil. Water. Air. Soil Pollut. 231, 539. https://doi.org/10.1007/s11270-020-04908-0

Tabassum, R.A., Shahid, M., Niazi, N.K., Dumat, C., Zhang, Y., Imran, M., Bakhat, H.F., Hussain, I., Khalid, S., 2019. Arsenic removal from aqueous solutions and groundwater using agricultural biowastes-derived biosorbents and biochar: a column-scale investigation. Int. J. Phytoremediation 21, 509–518. https://doi.org/10.1080/15226514.2018.1501340

Team, R., C., 2000. R language definition. Vienna Austria R Found. Stat. Comput.

Thouin, H., Norini, M.-P., Le Forestier, L., Gautret, P., Motelica-Heino, M., Breeze, D., Gassaud, C., Battaglia-Brunet, F., 2019. Microcosm-scale biogeochemical stabilization of Pb, As, Ba and Zn in mine tailings amended with manure and ochre. Appl. Geochem. 111, 104438. https://doi.org/10.1016/j.apgeochem.2019.104438

Trakal, L., Bingöl, D., Pohořelý, M., Hruška, M., Komárek, M., 2014. Geochemical and spectroscopic investigations of Cd and Pb sorption mechanisms on contrasting biochars: Engineering implications. Bioresour. Technol. 171, 442–451. https://doi.org/10.1016/j.biortech.2014.08.108

Trakal, L., Raya-Moreno, I., Mitchell, K., Beesley, L., 2017. Stabilization of metal(loid)s in two contaminated agricultural soils: Comparing biochar to its non-pyrolysed source material. Chemosphere 181, 150–159. https://doi.org/10.1016/j.chemosphere.2017.04.064

Wang, J., Wang, S., 2019. Preparation, modification and environmental application of biochar: A review. J. Clean. Prod. 227, 1002–1022. https://doi.org/10.1016/j.jclepro.2019.04.282

Zeng, G., Wan, J., Huang, D., Hu, L., Huang, C., Cheng, M., Xue, W., Gong, X., Wang, R., Jiang, D., 2017. Precipitation, adsorption and rhizosphere effect: The mechanisms for Phosphate-induced Pb immobilization in soils—A review. J. Hazard. Mater. 339, 354–367. https://doi.org/10.1016/j.jhazmat.2017.05.038

Zhou, R., Liu, X., Luo, L., Zhou, Y., Wei, J., Chen, A., Tang, L., Wu, H., Deng, Y., Zhang, F., Wang, Y., 2017. Remediation of Cu, Pb, Zn and Cd-contaminated agricultural soil using a combined red mud and compost amendment. Int. Biodeterior. Biodegrad. 118, 73–81. https://doi.org/10.1016/j.ibiod.2017.01.023

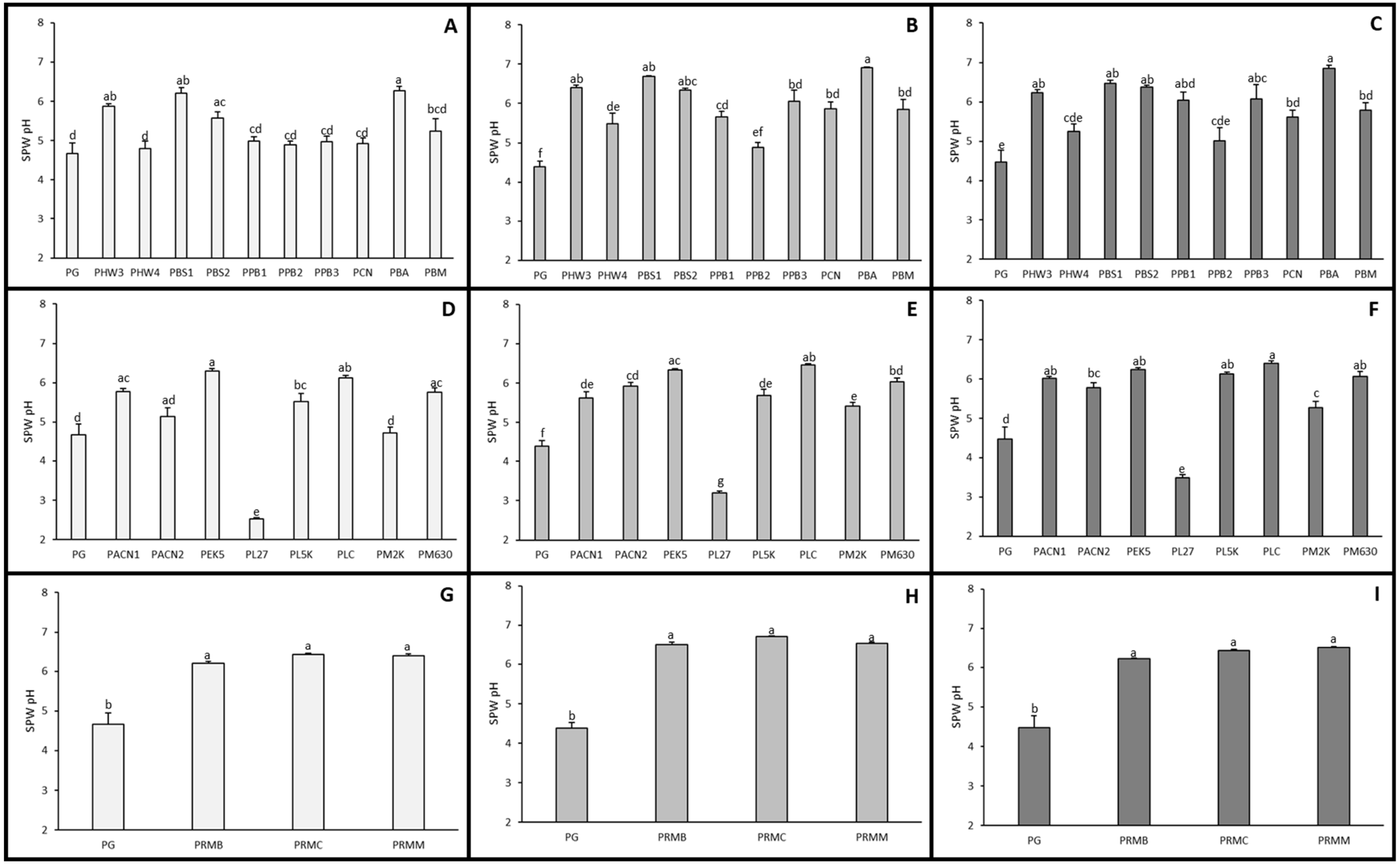

Figure 1: Soil pore water pH measured at T0 (light grey) (A, D, G), T14 (grey) (B, E, H) and T29 (dark grey) (C, F, I) in Pontgibaud technosol amended with different biochars (A, B, C), activated carbons (D, E, F) and redmuds (G, H, I). Letters indicate a significant difference between treatments ($p < 0.05$) ($n = 5$). The meaning of the treatment codes is given Table 2.

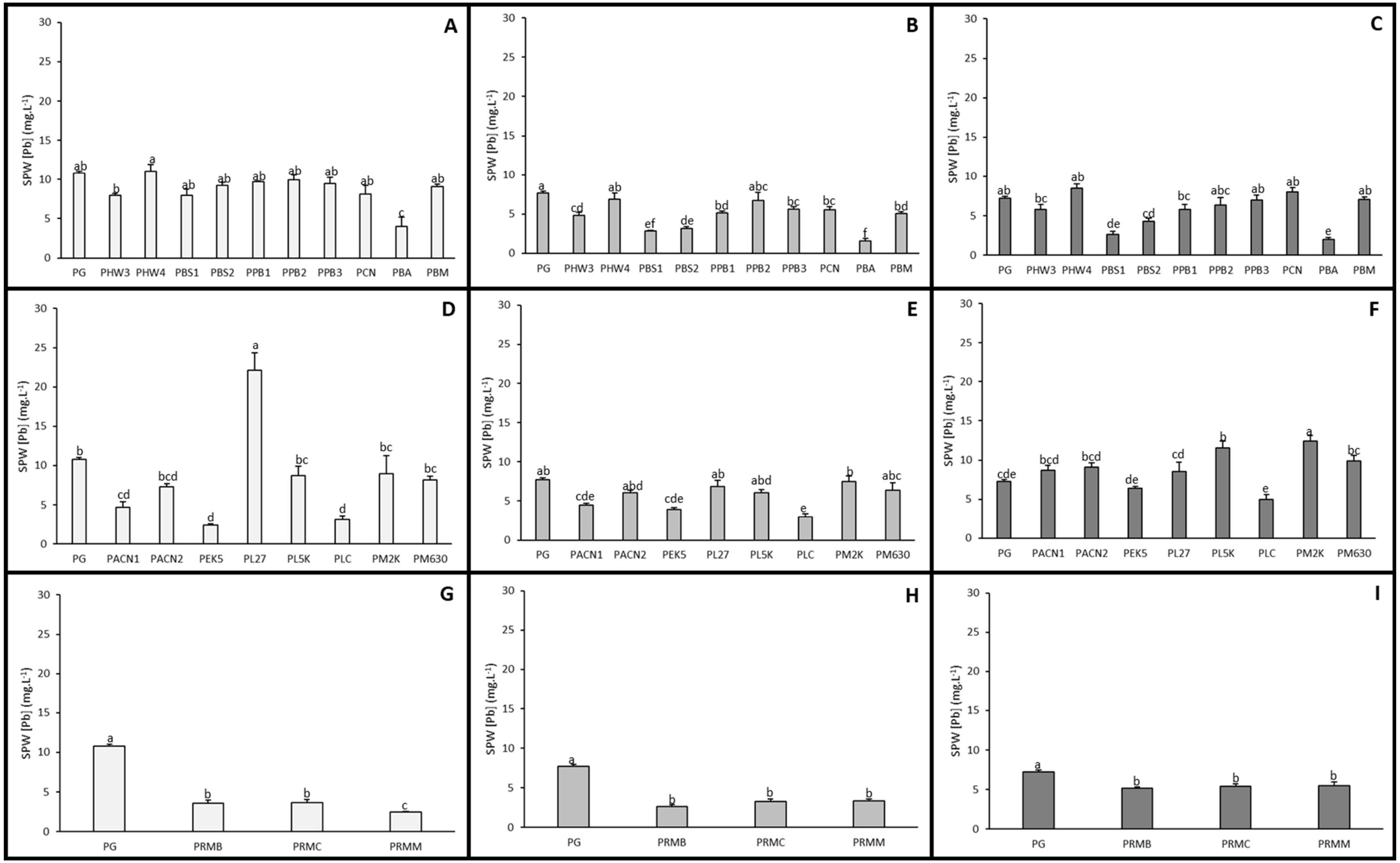

Figure 2: Soil pore water [Pb] (mg.L^{-1}) measured at T0 (light grey) (A, D, G), T14 (grey) (B, E, H) and T29 (dark grey) (C, F, I) in Pontgibaud technosol amended with different biochars (A, B, C), activated carbons (D, E, F) and redmuds (G, H, I). Letters indicate a significant difference between treatments ($p < 0.05$) ($n = 5$). The meaning of the treatment codes is given Table 2.

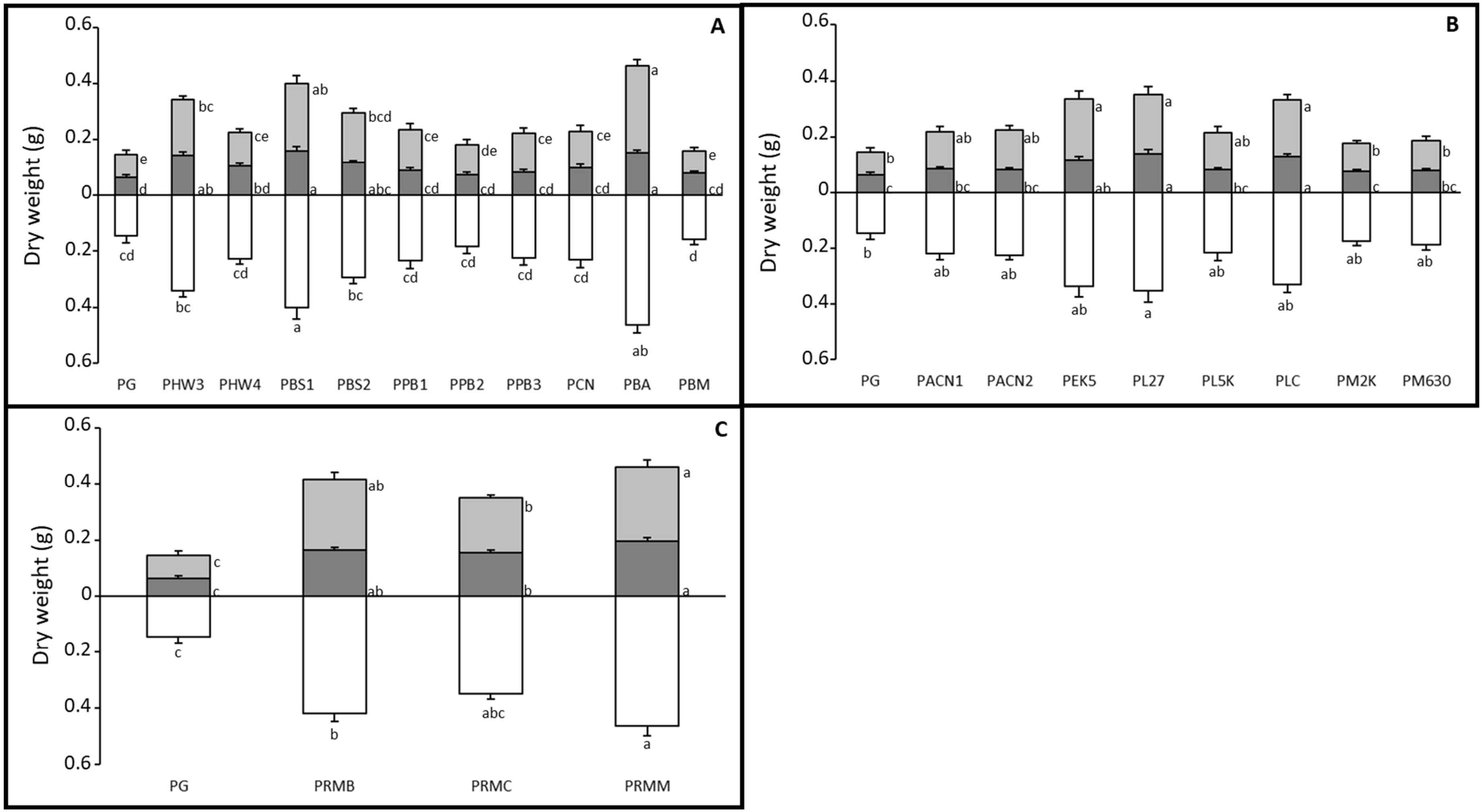

Figure 3: *Phaseolus vulgaris* leaf (light grey), stem (dark grey) and root (white) dry weight (g) after 15 days of growth on Pontgibaud technosol amended with different biochars (A), activated carbons (B) and redmuds (C). Letters indicate a significant difference ($p < 0.05$) ($n = 5$) between treatments. The meaning of the treatment codes is given Table 2.

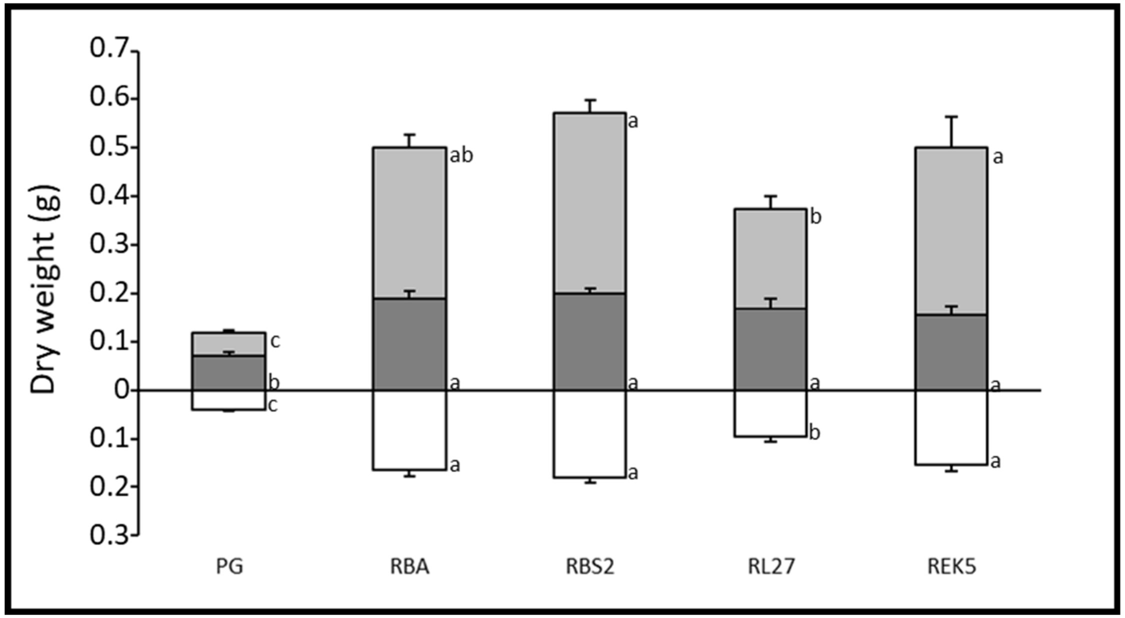

Figure 4: *Phaseolus vulgaris* leaf (light grey), stem (dark grey) and root (white) dry weight (g) after 15 days of growth on Pontgibaud (PG) technosol amended with 1% modified redmud in combinaison with 2 % BA biochar (RBA), 2% BS2 biochar (RBS2), 2% L27 activated carbon (RL27) or 2% EK5 activated carbon (REK5). Letters indicate a significant difference ($p < 0.05$) ($n = 5$).

Table 1. Codifications of the treatments of the experiment with the single amendment application.

Code	Treatment
PG	Non amended Pontgibaud technosol
PHW2	PG + 2% hardwood biochar (0.2-0.4 mm)
PHW3	PG + 2% hardwood biochar (0.5-1 mm)
PHW4	PG + 2% hardwood biochar (1-2.5 mm)
PBS1	PG + 2% oak bark-sapwood biochar (0.2-0.4 mm)
PBS2	PG + 2% oak bark-sapwood biochar (0.5-1 mm)
PPB1	PG + 2% pine bark biochar (0.2-0.4 mm)
PPB2	PG + 2% pine bark biochar (0.5-1 mm)
PPB3	PG + 2% pine bark biochar (1-2.5 mm)
PCN	PG + 2% coconut biochar (< 2 mm)
PBA	PG + 2% bamboo biochar
PBM	PG + 2% *Pseudotsuga* biochar inoculated with mycorrhizal fungi (2-3 mm)
PACN1	PG + 2% coconut steam activated carbon (0.25-0.59 mm)
PACN2	PG + 2% coconut steam activated carbon (0.42-0.168 mm)
PEK5	PG + 2% wood steam activated carbon
PL27	PG + 2% wood chemically activated carbon (0.59-2.38 mm)
PL5K	PG + 2% Lignite steam activated carbon (0.59-2.38 mm)
PLC	PG + 2% mineral base reactivated carbon (0.42-2.38 mm)
PM2K	PG + 2% mineral base steam activated carbon (0.42-0.168 mm)
PM630	PG + 2% agglomerate mineral steam activated carbon (0.42-0.168 mm)
PRMB	PG + 1% ochre
PRMC	PG + 1% bauxaline
PRMM	PG + 1% neutralized bauxaline

Table 2: Soil pore water physico-chemical properties measured at the beginning (T0) and at the end (TF) of the phytotoxicity test in Pontgibaud technosol (PG) amended with 1% modified redmud in combinaison with 2 % BA biochar (RBA), 2% BS2 biochar (RBS2), 2% L27 activated carbon (RL27) or 2% EK5 activated carbon (REK5). Letters indicate significant difference between treatments for each time ($p < 0.05$) (n = 5). Time effect is indicated by: * ($p < 0.05$). ** ($p < 0.01$). *** ($p < 0.001$) and ns (non-significant).

	pH			EC (µS.cm^{-1})			[As] (mg.L^{-1})			[Pb] (mg.L^{-1})		
	T0	TF	Time effect	T0	TF	Time effect	T0	TF	Time effect	T0	TF	Time effect
PG	4.7 ± 0.3 b	4.1 ± 0.1 c	ns	295 ± 17 c	507 ± 21 b	***	0.07 ± 0.01 c	0.14 ± 0.00 ab	***	10.8 ± 0.2 a	14.9 ± 0.8 a	***
RBA	6.9 ± 0.1 a	6.9 ± 0.1 a	ns	1681 ± 40 a	3932 ± 252 a	***	0.24 ± 0.00 bc	0.17 ± 0.01 b	**	2.2 ± 0.2 cd	1.9 ± 0.1 bc	ns
RBS2	6.6 ± 0.0 a	6.6 ± 0.2 ab	ns	1221 ± 40 b	3824 ± 367 a	**	0.25 ± 0.00 bc	0.15 ± 0.00 b	***	3.6 ± 0.5 bc	3.0 ± 0.4 b	ns
RL27	4.4 ± 0.4 b	6.7 ± 0.0 ab	**	1017 ± 60 b	3998 ± 312 a	**	5.51 ± 0.74 a	0.85 ± 0.17 a	**	1.9 ± 0.3 d	0.72 ± 0.1 c	**
REK5	6.6 ± 0.0 a	6.4 ± 0.1 b	**	1528 ± 65 a	3381 ± 332 a	**	0.30 ± 0.01 b	0.18 ± 0.01 b	***	4.5 ± 0.6 b	2.8 ± 0.2 b	ns

Table 3: Langmuir and Freudlich isotherm model constants, determined using sorption tests. Qm is the maximum sorption capacity while Ka and Kf are model constants.

	Langmuir isotherm			Freundlich isotherm		
	Qm	Ka	R^2	1/n	Kf	R^2
BA	92	0.0090	0.97	0.249	13.92	0.56
BS2	63	0.0038	0.91	0.282	6.47	0.94
EK5	156	0.0575	0.99	0.205	39.96	0.53
L27	162	0.0033	0.95	0.950	0.22	0.72
RMM	217	0.1685	0.99	0.248	57.11	0.48

BA = bamboo biochar, BS2 = oak bark sapwood biochar (0.5-1 mm), EK5 = steam activated carbon from vegetal biomass, L27 = chemically activated carbon from vegetal biomass, RMM = modified redmud.

Pontgibaud mine

Carbon-based amendments

Redmud

Phaseolus vulgaris growth