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Effect of Biochar and Amendments on Pb and As Phytotoxicity and Phytoavailability in a Technosol

*Romain Nandillon, Florie Miard, Manhattan Lebrun, Marie Gaillard, Stéphane Sabatier, Sylvain Bourgerie, Fabienne Battaglia-Brunet, and Domenico Morabito**

Phytostabilization has been proposed as a promising tool for long-term management of polluted sites. Optimization of the process efficiency involves choosing suitable amendments to allow both efficient plant growth and the immobilization of contaminants. The objectives of this study are to evaluate the effect of amendments on (i) the physicochemical properties of technosol and (ii) the mobility and phyto-availability of metal(loid)s. A dwarf bean growth test is conducted on technosols amended with compost, garden soil, slag, and biochar. The physicochemical properties of soil pore water (SPW) are determined as well as the phyto-available concentrations of metal(loid)s by simple extraction tests. All amendments used are able to increase SPW pH and electrical conductivity, allowing a decrease in the lead concentration in SPW by 90% and the lead phytoavailable part by 93%. However, for all amendments, SPW As concentration increased. Lastly, the amendments improve bean growth and tend to decrease the metal(oid) concentrations in aerial organs. As concentration in roots did not decrease whereas Pb concentration decreased. Metal(loid) concentrations of Pb accumulated in the aerial parts of beans and their extractable concentrations show a significant positive correlation with the extraction procedures. In contrast, the phytoavailable As shows a weak correlation with As concentrations in the aerial parts. The 1-M NH_4NO_3 extraction procedure is the most appropriate and provides the most useful indications of the phyto-availability for the studied elements.

1. Introduction

High concentrations of metal(loid)s in soils generated by mining activities could have negative effects on health when spread into the environment through wind and water erosion. One of the key factors in decreasing health risks and rehabilitating these polluted areas is a thorough understanding of the metal(loid) dynamics, not only within the soils, but also in their transfer to the environment. The rehabilitation of these sterile sites by adding amendments will improve their agronomic characteristics and stabilize the metal(loid)s in the soil, allowing the establishment of a plant cover which will limit the spread of metal(loid)s. Therefore, it is important to study the soil characteristics that control the phyto-availability of metal(loid)s and their accumulation in plants. Measuring the total toxic element contents in a soil will not give information about their potential mobilization and transfer to the environment. It is therefore necessary to study their bioavailability in order to estimate the potential danger linked to a possible run off of such toxic elements firstly into the hydrosphere, and then into living organisms such as plants. The final consequence will be a negative effect on human health due to entry into the food chain.[1] Therefore, it appears to be important to get more information on metal(loid) availability in soil and their uptake by aerial organs of plants.

The International Organization for Standardization (ISO) defines bioavailability as chemicals in soils that can be absorbed or metabolized by humans or ecological receptors, or that are available for interaction with biological systems (ISO 11074, 2005). The phyto-availability of metals in soils depends on the metal(loid) species and their distribution between the solid phase and the pore water due to the soil physico-chemical characteristics. Thus, many studies have been carried out on polluted soil to evaluate metal(loid) phyto-availability.[1,2] Moreover, a wide range of individual and sequential extraction schemes have been designed to evaluate the different forms of metal binding in soils using neutral salts ($CaCl_2$ and NH_4NO_3).[3]

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Plant ability to stabilize metal(loid)s in soils can be improved by using amendments that will reduce the mobility and bioavailability of metal(loid)s. Moreover, such amendments will contribute to the restoration of physical and chemical soil properties, as well as promoting efficient agronomical properties.[4–6] Several organic and inorganic amendments (compost, biosolids, lime, coal fly ash, phosphates, red mud, iron shot, and Fe/Mn/Al oxides) on polluted soils have already been proposed to enhance metal(loid) soil immobilization and biomass production.[6–8] Such bioavailability reduction is achieved by various complex processes, for example adsorption on mineral surfaces, formation of stable compounds with organic ligands, surface precipitation, and ion exchange.[6] Finally, the addition of organic-rich amendments such as compost, manure, various organic wastes, garden soil or biochar,[9,10] is commonly known to stimulate plant growth. However, these various amendments can add metal(loid)s to the soil. It is therefore essential to carry out preliminary analyses of the amendments, to make sure they are free of any contaminants.

The effect of organic matter on the bioavailability of metal(loid)s in a specific soil depends on amendment characteristics such as: (i) nature, (ii) microbial degradability, (iii) salt content, and (iv) effects on soil pH and redox potential.[11] Moreover, organic amendments may contain a high proportion of highly variable humified organic matter, which has a great capacity to interact with metal ions and to mobilize or immobilize metal(loid)s[12] by the formation of either more or less stable complexes.

Organic matter can also compete with As for sorption sites, and displace As(V) and As(III) from iron oxides (hematite).[13] It can influence the speciation of arsenic.[14]

However, the supply of organic matter is essential for plant growth. Thus, an effective amendment for arsenic immobilization must be used, as shown by Le Forestier et al.,[15] where alkaline slags (a by-product of the iron and steel industry containing metal oxides) have been used to improve contaminated acid soils by making metals less soluble through oxidation precipitation and adsorption on the slag surfaces. Amorphous Fe(III) hydroxide (ferrihydrite), which is present in slag, can be an effective sorbent for anions and cations. Possible adsorption of arsenite, As(III), As(V) and arsenate, on ferrihydrite are summarized by Jain et al.[16] The surface of the Fe hydroxide particles can be positively or negatively charged depending on the pH, allowing them to be amphoteric Fe hydroxide compounds. Leupin and Hug[17] observed that the slow and continuous release of Fe(II) in soils by the corrosion of iron provides ideal conditions for the oxidation of As(III) to As(V), which is easily adsorbed to iron hydroxides.

Among the organic amendments, biochar is considered an alkaline amendment able to increase soil pH, which induces Pb soil immobilization.[6,18] However, alkaline materials are described as undesirable in As-contaminated soils since they increase ion leaching, including As.[19] The same negative results on As mobilization have been observed when contaminated soil was amended with lime.[20] In contrast, Hartley et al.[19] found that lime could reduce arsenic leaching in moderation by the possible formation of As–Ca precipitant complexes (calcium hydrogenoarsenate, $CaHAsO_4$, and calcium arsenate, $Ca_3(AsO_4)_2$) under highly oxidizing and moderate pH conditions.[21]

In addition, the application of biochar improves plant growth by improving the agronomic properties of soils. Agegnehu et al.[22] demonstrated that addition of biochar (either alone or in combination with compost) improved peanut yield for site and pot experiments. These positive effects were associated with better plant N, P, and K uptake and an increase in soil-soluble organic carbon availability to soil microorganisms. Gartler et al.[23] demonstrated an efficient biochar effect on plants' Ca, Mg, and Zn availability, and on soil water retention capacity.

The objective of the present study was to evaluate the influence of a range of amendments on the phyto-availability of As and Pb, two toxic elements present in a mining technosol with contrasting biogeochemical behaviors. Biochar was used due to its capacity to immobilize Pb when added to a metal(loid) contaminated mining soil.[2] Slag amendment was associated to biochar in order to limit the As soil pore water availability which had increased levels in the presence of biochar. For this purpose, As and Pb mobility were measured in soil pore water (SPW) and in the soil salt extractable fraction of amended and non-amended soils. Phytotoxicity tests using bean germination were established, with plant dry weight, and As and Pb metal(loid) organ concentrations being measured and correlated to metal(loid) concentration in SPW.

2. Experimental Section

2.1. Soil Sampling

The studied site was in Roure-les-Rosiers, located in the Massif Central near Clermont-Ferrand (Saint-Pierre-le-Chastel (63), France) and was a former silver-lead extraction mine in the Pontgibaud mining district. The site is crossed by two rivers: the Veyssière, which constitutes the southern edge of the deposits, and the Faye which borders the northwest edge of the deposits before crossing them to join the Veyssière. The coordinates of the study area in Lambert II are: ⊗ X: 638147.54; ⊗ Y: 2087962.79.

The old mining site is subject to a semi-continental climate with hot summers (up to 40 °C), which can be marked by severe and localized thunderstorms, and snowy winters. On average, the Roure-les-Rosiers sector receives about 770 mm rainfall/year and is located at around 700 m.a.s.l.

The area mainly consists of deposits of silver-bearing lead ore that still contain a certain number of toxic elements (mainly lead $11655 \pm 448\ mg\ kg^{-1}$ and arsenic $483 \pm 13\ mg\ kg^{-1}$).

Surface soils (0–20 cm) were sampled with a stainless-steel shovel. All soil samples collected were carefully transferred to clean polyethylene bags before being transported to the laboratory. The collected soil samples were air dried (40 °C) and homogenized manually. One fraction was used to determine the physico-chemical properties of the soil while the other fraction was used for the chemical analysis of the metal(loid)s.

Samples for chemical analysis were screened first using a 2-mm mesh sieve to remove crude plant material.[1]

2.2. Soil Physicochemical Analysis

The pH and electrical conductivity were determined according to AFNOR NF T01-013, using a combined pH-EC meter (WTW, ProfiLine 1970i, Germany).

Total organic carbon (TOC) was determined in the soil samples by Rock-Eval pyrolysis (Rock-Eval 6 Turbo; Vinci Technologies, France).[24]

2.3. Amendments

The different types of amendments selected for this study were garden soil, slag, compost, and biochar (**Table 1**).

Garden soil was collected on the grounds of the University of Orleans, France. The garden soil allows an input of organic matter as well as essential elements. Its purchase cost is very low, generating a low financial impact. However, it can be of great heterogeneity, with soils of varying quality.

The base slag Valorseed 630 semolina was supplied by AXEREAL. Slag is a steel-based amendment used to improve soil characteristics in the context of agronomic studies (e.g., improvement of soil fertilization and soil pH in acid soils). This basic slag is composed of Ca, P, and metal oxides, and is an alkaline by-product of steel plants and waste incineration processes.

The compost used in this study was an Algoflash horticultural compost (NF U-44-551 growing medium) composed of peat moss, softwood bark compost, green compost, seaweed (Compo France, Roche-lez-Beaupré, France).

Biochar was supplied by La Carbonerie (Crissey, France). It was obtained from a slow pyrolysis (500 °C) of platelets and hardwood chips, composed of oak biomass, hornbeam, and beech. After pyrolysis, the product was passed through different sieves to recover a particle size range of 0.2–0.4 mm.

2.4. Soil Mixture Preparation

All types of amendments as well as the Pontgibaud technosol (Ps) were homogenized and sieved at 2 mm. Amendments (biochar (B), compost (C), garden soil (G), slag (S)) were mixed according to the combinations and the ratios are listed in **Table 2**.

A mixture of B with Ps was distributed into different batches for the following treatments: Ps + B, Ps + B + C, Ps + B + G, and Ps + B + C + S (Table 2). The different amendments were added, then the mixtures were divided into five replicates. A compost mixture was also prepared for treatments: Ps + C and Ps + C + S, and then each mixture was divided into five replicates. This procedure was applied to limit weighing errors and to have better sample representation. A total of 300 g of mixture was distributed into each pot. The pots were then placed outside for 30 days for soil equilibration. The seeds were then added and left for 13 days. The total duration of the experiment was 43 days.

Table 1. Physico-chemical properties of the amendments.

	Compost	Biochar	Garden soil	Slag
Granulometry (mm)	ND	0.2–0.4	<2	<2
pH	7.4 ± 0.0a	9.0 ± 0.0b	5.5 ± 0.0c	9.2 ± 0.0b
EC ($\mu S\,cm^{-1}$)	801 ± 24a	432 ± 2b	553 ± 2c	3266 ± 13d
WHC (%)	51 ± 1a	183 ± 3b	30 ± 2a	ND

ND, not determined; WHC, water holding capacity (% mass). Letters indicate significant difference ($p < 0.05$) ($n = 5$) between compost, biochar, garden soil, and slag.

Table 2. Treatment designations and percentage of different amendments per treatment.

Sample	Modality and amendment percentage (w/w)
Ps	Pontgibaud soil (Ps)
PsC	Ps + Compost (C) 5%
PsG	Ps + Garden soil (G) 5%
PsS	Ps + Slag (S) 2.5%
PsCS	Ps + C 5% + S 2.5%
PsB	Ps + Biochar (B) 2%
PsBC	Ps + B 2% + C 5%
PsBG	Ps + B 2% + G 5%
PsBS	Ps + B 2% + S 2.5%
PsBCS	Ps + B 2% + C 5% + S 2.5%

2.5. Germination Tests

Before being seeded, *Phaseolus vulgaris* "contender" variety seeds (dwarf bean) were sprouted in perlite. After 3 days the most homogeneous germinations were chosen and placed in the pots containing the technosol with different amendments. Two dwarf bean seedlings were sown in each pot and cultivated for 13 days in controlled conditions (16 h light/8 h darkness regime, 25 °C/21 °C with an approximate photon flux of 800 $\mu E\,m^{-2}\,s^{-1}$). The soil water holding capacity was kept between 55 and 65% by measuring the weight of each pot daily. It was adjusted with deionized water throughout the experimental period.

2.6. Pore Water Analysis

Soil pore water was collected twice during the growth experiment: at the beginning (T0) and at the end of the experiment, on day 13 (TF), before harvesting the plants. SPW sampling was performed using soil moisture samplers (Rhizon) (model MOM, Rhizosphere Research Products, Wageningen, the Netherlands), placed in pots at an angle of 45° over the entire depth of the pot (10 cm), and into the root system of the plant.

Collected SPWs were used directly to measure: (1) pH (pH-meter, FE20/EL20, Mettler-Toledo), (2) electrical conductivity (EC) (multimeter, WTW Multi 1970i, GEOTECH, Denver, Colorado), and (3) dissolved organic carbon (DOC), determined by a Teckmar–Dohrman Phoenix 8000 TOC analyzer. Total dissolved metal(loid) concentrations (As, Pb) were determined by inductively coupled plasma atomic emission spectroscopy

(ICP-AES) (ULTIMA 2, HORIBA, Labcompare, San Francisco, USA) after acidification, according to Bart et al.[25]

2.7. Plant Analysis

Plants were harvested 13 days after sowing. The above-ground plant tissues (primary leaves) were cut and rinsed thoroughly with double deionized water. Rinsed leaves were dried at 40 °C for 72 h before recording the dry matter yield. Roots were washed abundantly with tap water (twice) and washed once in distilled water to remove soil particles bound to roots. The bean organs were dried at 40 °C for 72 h before recording the dry matter yield, then ground with a laboratory grinder and digested using aqua regia with a pressurized vacuum microwave system (Multiwave 3000, Anton Paar, Austria).

The digestion program consisted of a gradual increase of 15 min at 180 °C, a digestion step of 15 min at 180 °C followed by a cooling step stopping at 55 °C for 15 min. After cooling to room temperature, the samples were added to 30 mL of ultra-pure water (18 MΩ cm^{-1}) and then filtered under vacuum on a 0.45-μm nitrocellulose membrane. ICP-AES measurements were performed from plant digestions to determine metal(loid) concentrations in dwarf bean organs.

2.8. As and Pb Pseudo-Total and Phytoavailable Concentrations

Soil was analyzed at the end of the experiment. The pseudo-total element concentrations were determined by aqua regia treatment with a solid/liquid ratio of 1/45.9 mL of aqua regia (HNO_3 (65%)/HCl (37%), 1:3 v/v) were added. The digestion program consisted of a gradual increase in temperature to 180 °C over 15 min, a digestion step of 15 min at 180 °C, followed by a 15 min cooling step. After cooling to room temperature, the samples were taken up in a volume of 50 mL with ultra-pure water (18 MΩ cm^{-1}) and then filtered on a 0.45-μm nitrocellulose membrane.

The As and Pb phytoavailable fractions were obtained as described by Qasim et al.[1] using two extractants: (i) $CaCl_2$ and (ii) NH_4NO_3. The acidified supernatants were stored at 4 °C until analysis. Metal(loid) concentrations were determined by ICP-AES (ULTIMA 2, HORIBA, Labcompare, San Francisco, USA).

2.9. Statistical Analysis

All tests were performed in five replicates and results are presented as mean ± standard error. The data were analyzed statistically using R statistical software Version 3.1.2 (R Development Core Team, 2009). Statistical analysis included calculation of Pearson's correlation coefficient to determine the relationships between the metal(loid) concentrations in the aerial parts of dwarf bean, and the extractable metal(loid) concentrations in soils for the different single extraction methods. The correlations were examined based on concentrations in dry plant weight. The level of significance was set at $p < 0.05$.

3. Results and Discussion

3.1. Effects of Amendments and Plants on Soil and SPW Properties

At the beginning of the experiment the pH of the technosol SPW was acidic (4.57 ± 0.08) and EC was 713 ± 11 μS cm^{-1} (**Table 3**). No significant difference was observed between T0 and TF for either the pH or EC of SPW.

When adding amendments to Pontgibaud soil (Ps), SPW pH and EC increased significantly ($p < 0.05$). However, converse effects were observed when comparing amendments. At the end of the experiment, garden soil addition was the least efficient in increasing SPW pH (5.02 ± 0.04). Whereas for compost, slag or biochar when added alone or in combination, the SPW pH value reached 7.5. When added alone to Ps, compost and biochar increased Pontgibaud SPW pH in the same way and did not induce statistical differences between treatments.

Pontgibaud SPW EC at the beginning and end of the experiment was ≈700 μS cm^{-1}. EC doubled when compost, garden soil or biochar were added to Ps, whereas slag amendment when added alone or in combination with the other three tested amendments caused an EC increase (1979–2408 μS cm^{-1}).

Such pH evolution was consistent with other studies.[26,27] Jones et al.[28] found a pH increase of a Cu-contaminated soil (clayey sand) correlating with biochar applications from 1 to 3%. In 2013, Chintala et al.[29] also observed an increase in pH and EC after a 2, 4, or 6% biochar application to an acid soil from a cultured Entisol. Moreover, Beesley et al.[27] showed that the pH of the pore water of a contaminated soil increased from 3.8 to 7.1, with addition of compost combined with biochar.

This increase in pH can be explained by two mechanisms: (i) the biochar alkaline pH induces a liming,[2] and (ii) the

Table 3. SPW physico-chemical characteristics (pH, EC, and DOC) in the different treatments, at the beginning (T0) and at the end of the experiment (TF) (13 days).

	pH		EC (μS cm^{-1})		DOC (mg L^{-1})
	T0	TF^{ns}	T0	TF^{ns}	TF
Ps	4.57 ± 0.08a	4.50 ± 0.03a	713 ± 11a	670 ± 24a	5.62 ± 0.30a
PsC	7.12 ± 0.05b	7.22 ± 0.04b	1331 ± 3b	1347 ± 9b	29.05 ± 4.40b
PsG	4.97 ± 0.01c	5.02 ± 0.04c	1422 ± 5c	1406 ± 8c	6.32 ± 0.45a
PsS	7.61 ± 0.04d	7.70 ± 0.04d	2408 ± 40d	2417 ± 44d	7.44 ± 2.33ad
PsCS	7.72 ± 0.02d	7.73 ± 0.02d	2137 ± 15e	2137 ± 15e	43.65 ± 3.86c
PsB	7.28 ± 0.02b	7.24 ± 0.02b	1307 ± 32b	1307 ± 32b	7.17 ± 1.09a
PsBC	7.52 ± 0.02e	7.57 ± 0.05e	1347 ± 9b	1344 ± 8b	27.25 ± 4.85b
PsBG	7.28 ± 0.02b	7.25 ± 0.02b	1406 ± 8c	1404 ± 10c	7.31 ± 0.56a
PsBS	7.56 ± 0.02f	7.60 ± 0.01f	2367 ± 54d	2367 ± 54d	11.91 ± 1.35d
PsBCS	7.75 ± 0.02d	7.76 ± 0.02d	1979 ± 26f	1979 ± 26f	47.91 ± 7.34c

(Ps): Pontgibaud soil, (PsC): Ps + compost (C) 5%, (PsG): Ps + garden soil (G) 5%, (PsS): Ps + slag (S) 2.5%, (PsCS): Ps + C 5% + S 2.5%, (PsB): Ps + biochar (B) 2%, (PsBC): Ps + B 2% + C 5%, (PsGB): Ps + B 2% + G 5%, (PsBS): Ps + B 2% + S 2.5%, (PsBCS): Ps + B 2% + C 5% + S 2.5%. Letters indicate a significant difference ($p < 0.05$) ($n = 5$). ns, no significant difference between T0 and TF.

incorporation of biochar and soil organic amendments allows the acidity of the soil solution to be reduced by the proton consumption reactions in the soil.[2,29]

The low pH increase measured on PsG can be attributed to the fact that the pH of the garden soil was close to that of the technosol and lower than that of the other amendments.

The EC of Ps was low $713 \pm 11\,\mu S\,cm^{-1}$ and was significantly increased by biochar addition $1307 \pm 32\,\mu S\,cm^{-1}$. To a lesser extent, the same results were observed by Molnàr et al.[26] as EC increased by 24% when 0.1% biochar of paper fiber feedstock was added to a sandy agricultural soil in Hungary.

The biochar and compost amendments significantly increased the TOC in the solid phases (Table S1, Supporting Information), whereas garden soil and slag did not. Pontgibaud DOC value was $5.62\,mg\,L^{-1}$. When G, S, or B were added alone to Ps no significant difference was observed between these treatments and Ps. Treatments with C showed the highest DOC levels from 29.05 ± 4.40 to $47.91 \pm 7.34\,mg\,L^{-1}$. When C was added alone to Ps or in combination with B, DOC increased significantly by about five times ($27.25 \pm 4.85\,mg\,L^{-1}$). This effect was amplified when S was added as a supplementary amendment and DOC reached a value of around $45\,mg\,L^{-1}$. Finally, when S and B were added to Ps, DOC was only doubled ($11.91 \pm 1.35\,mg\,L^{-1}$).

According to Beesley et al.[27] treatments including compost induced a significant increase of DOC in SPW. But it should also be noted that for all modalities containing slag associated with one or more amendments (B and C), DOC levels were significantly higher than PsS from 11.91 ± 1.35 to $43.65 \pm 3.86\,mg\,L^{-1}$. The influence of biochar on the DOC in SPW was weak. Whether biochar was applied on field or on pot studies, Jones et al.[28] showed that biochar amendment did not induce variations in SPW DOC concentrations, even though biochar is mainly composed of carbon. This is explained by the biochar carbon being refractory to physico-chemical or micro-organisms degradation. It has been demonstrated that the biochar carbon pool is relatively stable and insoluble for centuries and could not be remobilized.[27] The modalities containing compost demonstrated a higher DOC rate, which could be explained by the fact that even though the compost is mainly composed of refractory humified material it is also composed of fresh organic matter, and therefore very labile.[30] Compost provides more labile organic carbon than biochar, which would explain a higher DOC concentration.

The presence of slag mixed with biochar or compost increases SPW DOC content, which means that the minerals brought in by the slag could compete with some organic matter, inducing the solubilization of specific carbonic chemical groups released in SPW.[30] However, it must be mentioned that in some studies a decrease in DOC was observed when biochar was used as an amendment.[2] Hass et al.[31] proposed two mechanisms to explain such a phenomenon: (i) specific biochar structure could bind to carbon and (ii) biochar could improve soil microorganism activity inducing a mineralization of the soluble carbon organic matter. Because of the short experimental period it was impossible to stimulate soil microbial activities, which is no SPW DOC decrease was observed when biochar was added to Ps.

3.2. Effects of Amendments on Soil and SPW Physico-Chemical Characteristics

Measuring metal(loid) concentration in the SPW makes it possible to estimate the highly mobilizable metal(loid) part of a soil, and therefore the most easily phyto-available for plants growing in such conditions. Phyto-availability tests were done by measuring the metal(loid) fractions in NH_4NO_3 and $CaCl_2$ as selective extractants. A correlation between selective extractants, and the metal(loid) concentration in organs will determine which selective extractant best reflects the metal(loid) SPW fraction available for plants.

3.2.1. Arsenic Concentrations in SPW and Selective Extractions

At T0 all amendments induced a significant As concentration increase in the SPW. The lowest value ($0.010 \pm 0.00\,mg\,L^{-1}$) was observed when biochar was added alone to Ps and corresponded to a 27% increase. However, when all amendments were added to Ps (PsBCS), As concentration in SPW was the most important compared to the other treatments and corresponded to 140% of the concentration measured in Ps. For all treatments, arsenic concentration was significantly less important at TF than T0, and no differences between Ps, PsC, and PsS were observed at the end of the experiment. At TF for the PsBCS treatment, arsenic concentration was strongly mobilized, up to 480% compared to Ps. This As concentration increase was positively correlated to pH (0.49) and DOC (0.87) (Table 5). It should also be noted that at TF for most treatments, As concentrations in the SPW were below the environmental release standard stated at $0.1\,mg\,L^{-1}$ (Legifrance), and that garden soil amendment resulted in a decrease in SPW As concentration to almost $0\,mg\,L^{-1}$.

The results of selective extractants, which were used to estimate the arsenic phyto-availability, demonstrated a higher arsenic extraction when using NH_4NO_3 compared to $CaCl_2$. The difference in favor of NH_4NO_3 was between 1.6- and 5.3-fold for PsC and PsBS, respectively (**Table 4**). No significant correlation was demonstrated between SPW As concentration and As-selective extractant, which were -0.02 for $CaCl_2$ and 0.52 for NH_4NO_3. When $CaCl_2$ was applied to biochar Ps amended soil, only 0.03% of total soil As was extracted, except for the PsBCS treatment, which released 0.06% of total As. With NH_4NO_3, the lowest arsenic mobilization was observed in the PsC treatment, with 0.10% of total soil As. This value increased with the other treatments (PsG, PsS, PsCS, PsBS, and PsBCS), which exhibited extraction proportions of $\geq$0.17% of total soil As. Whereas for PsB, PsBC and PsBG, NH_4NO_3 gave the same proportion of available As (0.14%) as when NH_4NO_3 was applied to Ps. It should be emphasized, however, that a positive correlation was found between the As concentration in SPW and DOC (0.87), demonstrating that there is a dependence between arsenic concentrations in SPW and soil organic matter.

Arsenic, unlike cationic metals (Cu, Zn, Pb, Cd, etc.), is present in the form of an oxyanion in solution and its mobility in soils increases with increasing soil pH. It is well known that arsenic adsorption generally decreases with increasing pH values,[27,32] as arsenic often binds to iron oxides, which are

Table 4. As and Pb concentrations in SPW (at the beginning (T0) and at the end of the experiment (TF)) and As and Pb phyto-availability using selective extractants ($CaCl_2$ or NH_4NO_3).

	SPW				Phytoavailability			
	As (mg L^{-1})		Pb (mg L^{-1})		As (%)		Pb (%)	
	T0	TF**	T0	TF**	$CaCl_2$	NH_4NO_3**	$CaCl_2$	NH_4NO_3**
Ps	0.08 ± 0.00a	0.02 ± 0.01a	16.15 ± 2.83a	13.20 ± 0.13a	0.07 ± 0.01a	0.14 ± 0.01a	4.11 ± 0.14a	12.37 ± 1.21a
PsC	0.13 ± 0.02b	0.03 ± 0.00a	0.55 ± 0.08b	0.18 ± 0.02b	0.06 ± 0.01a	0.10 ± 0.01b	0.26 ± 0.03b	2.31 ± 0.33b
PsG	0.11 ± 0.01b	0.00 ± 0.00b	15.90 ± 1.49a	13.28 ± 0.63a	0.06 ± 0.01a	0.18 ± 0.01c	4.12 ± 0.08a	9.86 ± 1.35c
PsS	0.13 ± 0.01b	0.03 ± 0.00a	0.46 ± 0.10bc	0.23 ± 0.04bcd	0.05 ± 0.01a	0.18 ± 0.00c	0.03 ± 0.00c	0.11 ± 0.02d
PsCS	0.17 ± 0.01c	0.07 ± 0.00c	0.44 ± 0.03bc	0.29 ± 0.01d	0.06 ± 0.00a	0.17 ± 0.01c	0.02 ± 0.00c	0.03 ± 0.00e
PsB	0.010 ± 0.00d	0.01 ± 0.00b	0.36 ± 0.04bc	0.43 ± 0.06c	0.03 ± 0.01b	0.14 ± 0.00a	1.08 ± 0.06d	3.65 ± 0.23f
PsBC	0.14 ± 0.01b	0.07 ± 0.01c	0.30 ± 0.03b	0.16 ± 0.00bc	0.03 ± 0.01b	0.14 ± 0.01a	0.07 ± 0.01e	0.03 ± 0.01e
PsBG	0.11 ± 0.01d	0.01 ± 0.00b	0.58 ± 0.14bc	0.93 ± 0.06e	0.03 ± 0.01ab	0.13 ± 0.00a	0.58 ± 0.15f	1.61 ± 0.14g
PsBS	0.13 ± 0.01b	0.04 ± 0.01d	0.41 ± 0.00c	0.32 ± 0.17bcd	0.03 ± 0.00b	0.16 ± 0.02ac	0.03 ± 0.00c	0.05 ± 0.02e
PsBCS	0.19 ± 0.01e	0.12 ± 0.02e	0.37 ± 0.03bc	0.25 ± 0.01bd	0.06 ± 0.01a	0.20 ± 0.01c	0.02 ± 0.00c	0.06 ± 0.01e

(Ps): Pontgibaud soil, (PsC): Ps + Compost (C) 5%, (PsG): Ps + Garden soil (G) 5%, (PsS): Ps + Slag (S) 2.5%, (PsCS): Ps + C 5% + S 2.5%, (PsB): Ps + Biochar (B) 2%, (PsBC): Ps + B 2% + C 5%, (PsGB): Ps + B 2% + G 5%, (PsBS): Ps + B 2% + S 2.5%, (PsBCS): Ps + B 2% + C5% + S 2.5%. Letters indicate a significant difference ($p < 0.05$) ($n = 5$). **, significant difference between T0 and TF or between selective extractants $CaCl_2$ and NH_4NO_3.

subject to a decrease in positive surface charge when pH increases. The mobility, toxicity and availability of As in the environment are strongly influenced by soil physico-chemical properties and are mainly controlled by adsorption–desorption processes.[32] Changes in organic matter can directly or indirectly alter the distribution and availability of metals in soils.[7] The effect of organic residues on arsenic mobility and bioavailability depends on the type of soil and soil characteristics (EC, pH, and degree of humification).[11] Fitz and Wenzel[33] reported a higher As solubility in soils when pH increased from pH 3 to 8. This may also mean that the conditions induced by the addition of biochar to the soils may control the mobility of As and Pb, regardless of the capacity of the biochar as the sorbent.

The addition of compost can increase the mobility and leaching of metal(loid)s, and in particular arsenic.[20] Strong increases in the arsenic concentration of the SPW of compost-modified soils have been observed, probably because DOC competes with arsenic for sorption sites on Fe oxides and Al, resulting in increased mobility of arsenic.[7,20] The compost may also contain soluble phosphorus, which can displace arsenic from organic and inorganic binding sites.[7] In addition, Moreno-Jiménez et al.[34] observed that the mobilization of arsenic, Cu and Se after application of olive plant waste compost to flooded soils could be attributed to increased concentrations of DOC in interstitial water. On the other hand, Cao and Ma[35] used compost to remediate soils contaminated with chromium-copper arsenate and reported a positive effect on arsenic adsorption. Beesley et al.[36] found no statistically significant correlation between As and DOC concentrations in SPW of a compost-amended soil, indicating that DOC did not drive mobilization of As in this soil. The correlation between SPW As and DOC probably depends on the specific properties of the amended soil. The results obtained on amended Pontgibaud soil are in agreement with those of Moreno-Jiménez et al.[34] who also suggested that the phosphorus brought by compost could in part be responsible for the mobilization of arsenic. The high mobilization of As in treatments with slag may also be linked to the large amount of phosphorus supplied by this amendment. The use of slag was intended to reduce the mobility of As thanks to its content of iron and aluminum oxy(hydro)xides. Moreover, metal oxides and clay minerals in the soils bind arsenic.[37] However, the combination of the slag with the compost and the biochar in fact induced arsenic mobilization. This was due to the multiple competition phenomena between organic matter and arsenic for sorption on the Fe oxy(hydro)xides, thanks to the phosphorus supplied by the slag, and the increased solubilization of organic carbon in SPW in the presence of slag.

3.2.2. Lead Concentrations in SPW and Selective Extractions

At T0, all treatments (Table 4), apart from the treatment with garden soil, decreased the total Pb content of the SPW by 97% when compared to Pontgibaud soil. For Ps and PsG, the SPW Pb concentration was almost the same at the beginning and end of the experimental period and corresponded approximately to 14.6 mg L^{-1}, whereas for the other treatments the SPW Pb concentration was between 0.1 and 0.9 mg L^{-1}.

Concerning the selective extraction, treatments can be classified into three groups: (i) Ps and PsG, which demonstrated the highest Pb phyto-available fraction (4% for $CaCl_2$ and 11% for NH_4NO_3); (ii) PsC, PsB, and PsBG, which demonstrated a Pb phyto-available fraction ranging from 0.2 to 1% for $CaCl_2$ and 1.6 to 3.6% for NH_4NO_3; (iii) PsS, PsCS, PsBC, PsBS, and PsBCS treatments, in which almost no Pb was extracted neither by $CaCl_2$ nor NH_4NO_3. Finally, the correlation tests (−0.99) showed that there was a strong and negative correlation between SW pH and lead availability (**Table 5**).

Compost, biochar, and slag have high concentrations of basic cations. Compost and biochar also have high organic matter

Table 5. Correlations between pH, EC, DOC, As concentration, Pb concentration, As $CaCl_2$ or NH_4NO_3 selective extractant, Pb $CaCl_2$ or NH_4NO_3 selective extractant, organs dry weight and organs metal(loid)s concentrations.

	SPW						Selective extractant T0				Dry weight TF		Organs metal(loid)s concentrations TF			
	pH T0	DOC TF	[As] T0	[As] TF	[Pb] T0	[Pb] TF	As $CaCl_2$	As NH_4NO_3	Pb $CaCl_2$	Pb NH_4NO_3	AP	R	$[As]_{AP}$	$[As]_R$	$[Pb]_{AP}$	$[Pb]_R$
SPW pH	1.00	0.49	0.68	0.47	−0.98	−0.98	0.32	−0.03	−0.98	−0.99	0.95	0.91	0.31	−0.16	−0.75	−0.96
SPW DOC	0.49	1.00	0.88	0.87	−0.43	−0.45	0.04	0.45	−0.52	−0.49	0.45	0.51	0.10	0.01	−0.74	−0.50
SPW [As] T0	0.68	0.88	1.00	0.90	−0.58	−0.59	−0.02	0.52	−0.68	−0.71	0.69	0.74	0.30	0.27	−0.94	−0.66
SPW [As] TF	0.47	0.87	0.90	1.00	−0.39	−0.40	−0.01	0.59	−0.50	−0.49	0.48	0.54	0.32	0.24	−0.80	−0.43
SPW [Pb] T0	−0.98	−0.43	−0.58	−0.39	1.00	1.00	−0.32	0.16	0.98	0.96	−0.93	−0.85	−0.29	0.31	0.64	0.96
SPW [Pb] TF	−0.98	−0.45	−0.59	−0.40	1.00	1.00	−0.32	0.17	0.98	0.96	−0.93	−0.85	−0.27	0.31	0.65	0.95
As $CaCl_2$ selective extractant T0	0.32	0.04	−0.02	−0.01	−0.32	−0.32	1.00	0.00	−0.20	−0.23	0.07	0.15	−0.37	−0.18	0.01	−0.29
As NH_4NO_3 selective extractant T0	−0.03	0.45	0.52	0.59	0.16	0.17	0.00	1.00	0.12	0.01	−0.04	0.01	0.40	0.47	−0.41	0.01
Pb $CaCl_2$ selective extractant T0	−0.98	−0.52	−0.68	−0.50	0.98	0.98	−0.20	0.12	1.00	0.98	−0.97	−0.90	−0.31	0.21	0.76	0.94
Pb NH_4NO_3 selective extractant T0	−0.99	−0.49	−0.71	−0.49	0.96	0.96	−0.23	0.01	0.98	1.00	−0.97	−0.92	−0.34	0.10	0.80	0.96
Aerial parts dry weight	0.95	0.45	0.69	0.48	−0.93	−0.93	0.07	−0.04	−0.97	−0.97	1.00	0.93	0.42	−0.07	−0.79	−0.89
Roots dry weight	0.91	0.51	0.74	0.54	−0.85	−0.85	0.15	0.01	−0.90	−0.92	0.93	1.00	0.20	0.16	−0.82	−0.79
$[As]_{AP}$	0.31	0.10	0.30	0.32	−0.29	−0.27	−0.37	0.40	−0.31	−0.34	0.42	0.20	1.00	−0.12	−0.34	−0.33
$[As]_R$	−0.16	0.01	0.27	0.24	0.31	0.31	−0.18	0.47	0.21	0.10	−0.07	0.16	−0.12	1.00	−0.30	0.28
$[Pb]_{AP}$	−0.75	−0.74	−0.94	−0.80	0.64	0.65	0.01	−0.41	0.76	0.80	−0.79	−0.82	−0.34	−0.30	1.00	0.71
$[Pb]_R$	−0.96	−0.50	−0.66	−0.43	0.96	0.95	−0.29	0.01	0.94	0.96	−0.89	−0.79	−0.33	0.28	0.71	1.00

T0, beginning of the experiment; TF, end of the experiment (13 days); AP, aerial part; R, root.

content. These characteristics result in an increase in pH and cationic exchange capacity.[38] The increase in pH therefore increased the surface charges of soil particles and thus the retention of metals.[38,39] Humified organic matter, which has a high capacity to interact with metal ions and mobilize or immobilize metals,[12] could reduce their mobility (and therefore their bioavailability) in the soil profile through the formation of more or less stable complexes.[7] Moreover, biochar has a negative charge, allowing electrostatic attraction, and has a large specific surface.[9,40] It is well known that the mobility of metal is strongly influenced by the adsorption phenomena that connect them to biochar surfaces.[7]

Amendments can immobilize metals by three mechanisms: (i) adsorption of metals at highly accessible sites on the surface of soil components or aluminosilicates; (ii) precipitation with oxides of Al, Fe, or Mn; and (iii) formation of minerals (such as metal silicates) and diffusion through mineral surfaces.[41] These different properties allow the implementation of different mechanisms, which can make metals unavailable for absorption by plants through changes to SPW pH and lead availability.

Compost, biochar, and slag have high basic cation concentrations. Compost and biochar also have high organic matter content. These characteristics result in a CEC and pH increase.[38] Which modify the surface charges of soil particles and thus the retention of metals.[38,39] Compost has also been shown to influence the availability of metal(loid)s by binding them to humic acids.[7]

3.3. Plant Dry Weight and Metal(loid) Uptake

The root biomass for beans grown on Ps was 39.9 mg. All treatments improved the root biomass. Plants in the first group, composed of PsS, PsCS, PsBC, PsBG, PsBS, and PsBCS, did not demonstrate significant statistical differences in terms of root biomass. Their dry weights ranged from 181.2 to 255.4 mg. The second group, which was composed of PsG, PsB, and PsC, had a root biomass between 62.9 and 145.1 mg (**Figure 1**).

Concerning the biomass of the aerial parts, the lowest value was observed on Ps (236.3 mg), and no difference was observed for the PsG treatment. However, for the other studied treatments the dry weight was significantly increased compared to Ps and was in fact doubled (500 mg) (Figure 1).

In this study, addition of amendments was beneficial for plant growth. This can be explained by the improvement of the physical properties of the soil, in particular the water retention capacity, notably by the addition of organic amendments.[42] Moreover, organic matter, provided by compost improved the N, P, K nutrient cycle,[43] allowing a better plant growth, as observed by Marques et al.[43] on *Solanum nigrum*.

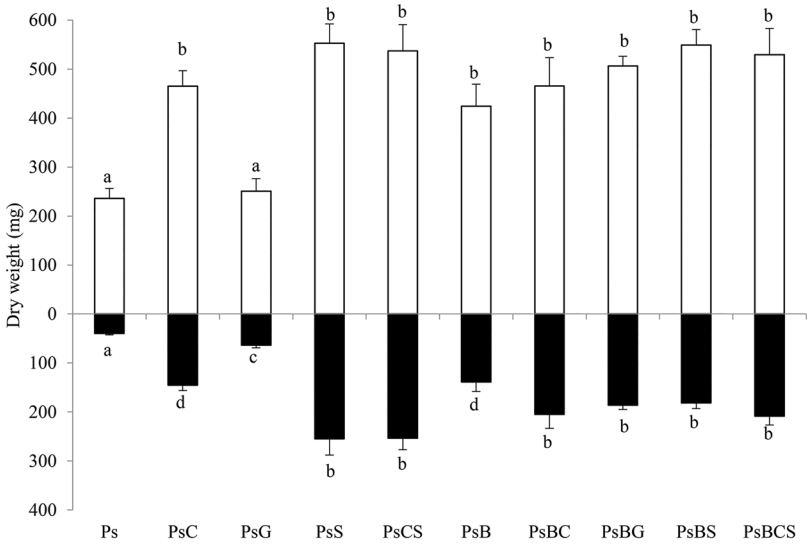

Figure 1. Dry weight (g) of dwarf beans organs (aerial parts (white column), roots (black column)) at the end of the experiment (13 days). (Ps): Pontgibaud soil, (PsC): Ps + compost (C) 5%, (PsG): Ps + garden soil (G) 5%, (PS): Ps + slag (S) 2.5%, (PsCS): P + C 5% + S 2.5%, (PsB): Ps + biochar (B) 2%, (PsBC): Ps + B 2% + C 5%, (PsGB): Ps + B 2% + G 5%, (PsBS): Ps + B 2% + S 2.5%, (PsBCS): Ps + B 2% + C 5% + S 2.5%. Results are expressed as the mean value and standard error ($n = 10$), letters on bar graphs indicate a significant difference ($p < 0.05$).

The beneficial effect provided by biochar on root biomass (3.5-fold) and on aerial part biomass (1.8-fold) was already observed by Puga et al.[40] on *Mucuna aterrima* when up to 5% of cane straw biochar was applied to an old zinc mining area.

Two mechanisms can be proposed to explain the plant growth improvement induced by the addition of biochar in metal(loid) contaminated soil: (i) biochar could improve water retention capacity[22] and (ii) biochar could increase the pH of the soil[44] due to its alkalinity, also demonstrated by Lebrun et al.[2] This is confirmed by the positive correlation between root biomass (0.91), aerial biomass (0.95) and pH value.

Concerning the slag, Prado et al.[45] observed that calcium limestone and basic slag applied in sugar cane fields generated a beneficial effect in correcting soil acidity. Moreover, Le Forestier et al.[15] showed a link between the increase of soil pH and the decrease of acid-soluble and oxidizable fractions in slag modified soils. However, in the present work, by comparing PsS and PsB modalities, a better root biomass production was observed for PsS in spite of Pb being less present in SPW than As. This observation could be explained by the higher biochar sorption capacity which could reduce plant nutrient availability and thus soil fertility.[46]

The combination of amendments allowed a better improvement of the bean root dry weight when Ps was amended with individual amendments (C, G, B) except when S was added to Ps. Moreover, among the treatments composed of Ps and only one amendment, only compost and biochar reduced the SPW Pb concentration (Table 4), although the pH in SPW was the same as the one measured on multi-amended Ps. The combination of amendments probably improved root growth by providing more available nutrients than individual amendments.

Moreover, the increase in As concentration in SPW linked to the addition of amendments did not have any negative effects on bean growth, probably due to the fact that arsenic concentration remained below the plant toxicity threshold.

Dwarf beans growing for 13 days in soil amended differently showed an accumulation of metal(loid)s in the aerial and roots parts of plants in variable amounts (**Figure 2** and **3**).

In the present study, there were differences in metal(loid) concentrations between the roots and the aerial parts of plants, but no distinction between leaves and stems was observed. For all treatments metal(loid) concentrations were higher in the roots than in the aerial parts of the beans. For Pb it corresponded to 0.25 g kg^{-1} in aerial part and 6 g kg^{-1} for the roots, whereas for As it corresponded to 5 mg kg^{-1} in aerial part and 200 mg kg^{-1} for the roots.

Regardless of the amendment used, arsenic concentrations in the aerial parts of the beans ranged from 2.5 to 14.5 mg kg^{-1}, and in the roots between 110 and 290 mg kg^{-1}. For lead, the range was 0.10–0.36 g kg^{-1} and 4.8–24.5 g kg^{-1} for aerial and root parts, respectively.

In detail, for As concentrations in aerial parts, there were no significant differences between Ps and PsG treatments, with values of 14.5 ± 3.1 and 11.2 ± 1.5 mg kg^{-1}, respectively. These concentrations were 4.2 times higher than those observed in the aerial parts of the beans grown on the other amended soils. Finally, the As concentrations found in the aerial parts of PsC, PsS, PsCS, PsB, PsBC, PsBG, PsBS, and PsBCS were below the value observed by Mench et al.[47] and Carbonell-Barrachina et al.[48] for aerial parts of beans grown on control soil, 0.38 and 5.2 mg kg^{-1}, respectively.

Pb concentration in roots of beans grown on Pontgibaud soil was 68 times higher than in aerial parts, with root Pb concentration being 24.5 g kg^{-1}, and Pb concentration in aerial parts being 0.4 g kg^{-1} (Figure 3). For all treatments, garden soil amendment decreased root Pb concentration by 1.4-fold compared to Ps whereas the other treatments decreased Pb roots concentration 4.2-fold. For the aerial parts (Figure 3) when biochar or garden soil were added alone or in combination, Pb concentration was no different to that measured on plants grown on Ps. Moreover, when amendments added to Ps containing S or a combination of B and C, Pb concentration in aerial parts was four times lower than that measured in aerial parts of beans grown on Ps.

Finally, SPW Pb concentrations were significantly correlated with root tissue Pb concentration (0.95, Table 5). However, no significant correlations could be observed for arsenic concentrations in SPW and root tissues (0.24). The fact that Pb and As are mainly found in plant roots has been already emphasized by Lebrun et al.[2] who found the same results when *Populus* or *Salix* trees were grown on metal-contaminated soils (Co, Cu, Pb, and Zn).

The addition of a single amendment can result in reduced concentrations of metal(loid)s in plant tissues, but can also lead to the accumulation of metal(loid)s.[38] When added to

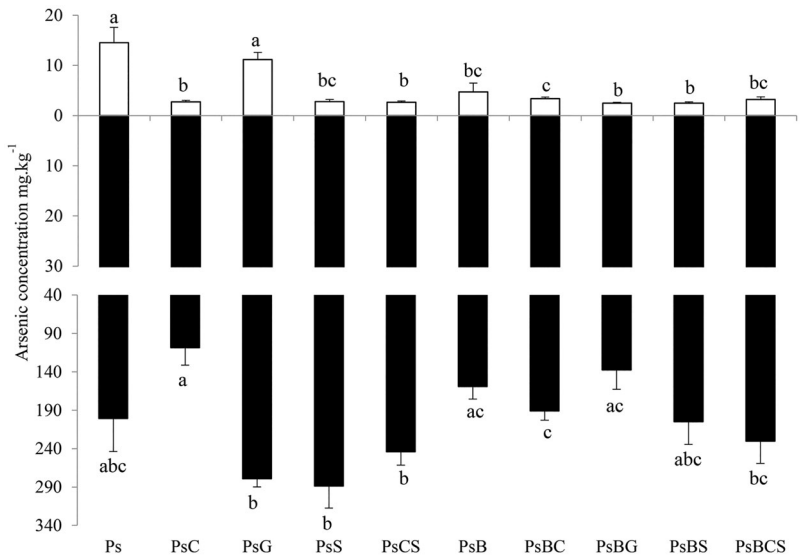

Figure 2. Arsenic concentrations (mg kg^{-1}) in dwarf bean organs (aerial parts (white column), roots (black column)) at the end of the experiment (13 days). (Ps): Pontgibaud soil, (PsC): Ps + compost (C) 5%, (PsG): Ps + garden soil (G) 5%, (PS): Ps + slag (S) 2.5%, (PsCS): P + C 5% + S 2.5%, (PsB): Ps + biochar (B) 2%, (PsBC): Ps + B 2% + C 5%, (PsGB): Ps + B 2% + G 5%, (PsBS): Ps + B 2% + S 2.5%, (PsBCS): Ps + B 2% + C 5% + S 2.5%. Results are expressed as the mean value and standard error ($n = 10$), letters on bar graphs indicate a significant difference ($p < 0.05$).

Pontgibaud soil, the amendments allow a reduction of arsenic accumulation in the aerial parts. The chemical composition and sorption properties of soil influence the mobility and bioavailability of metals. Generally, only a fraction of metal(loid)s in soils is bioavailable for uptake by plants. Metal(loid)s in soils are generally classified into three categories according to their bioavailability: (i) readily bioavailable (Cd, Ni, Zn, As, Se, Cu); (ii) moderately bioavailable (Co, Mn, Fe); and (iii) less bioavailable (Pb, Cr, U).[49]

Gupta and Sinha[3] have shown that the process of metal(loid) accumulation in plants depends on the concentration of available metals in soils, their mobility, and the plant species that grow on these soils. The metal(loid)s considered to be available for plant uptake are those which exist as soluble components in the soil solution or which are readily desorbed or solubilized by root exudates, often representing only a small part of the total ions,[1] as found in the present study.

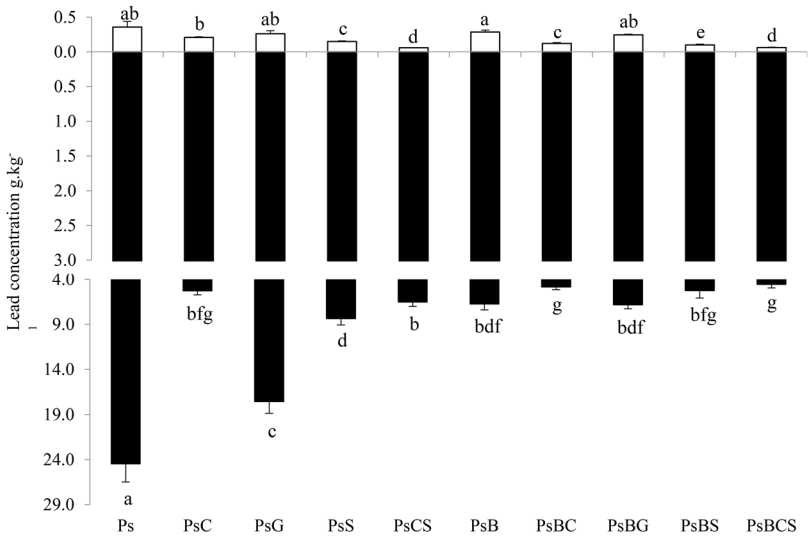

Figure 3. Lead concentrations (g kg^{-1}) in dwarf bean organs (aerial parts (white column), roots (black column)) at the end of the experiment (13 days). (Ps): Pontgibaud soil, (PsC): Ps + compost (C) 5%, (PsG): Ps + garden soil (G) 5%, (PS): Ps + slag (S) 2.5%, (PsCS): P + C 5% + S 2.5%, (PsB): Ps + biochar (B) 2%, (PsBC): Ps + B 2% + C 5%, (PsGB): Ps + B 2% + G 5%, (PsBS): Ps + B 2% + S 2.5%, (PsBCS): Ps + B 2% + C 5% + S 2.5%. Results are expressed as the mean value and standard error ($n = 10$), letters on bar graphs indicate a significant difference ($p < 0.05$).

4. Conclusion

The soil of the former mining site used for this study (Pontgibaud soil) presents high concentrations of As and Pb, which inhibit the growth of endemic plants and induce a high risk of the spread of environmental metal(loid)s. However, the addition of various amendments (compost, biochar or slag) improves the physico-chemical characteristics of the soil by immobilizing metals, which allowed plant growth, and could therefore reduce the environmental risks associated to these contaminated soils.

In soil ecosystem surveys, consideration should be given to the phyto-available fraction of metals that may be transferred to the trophic chain, irrespective of the total metal(loid) content. Various extraction agents were used to assess the phyto-availability of the metal(loid)s. The $CaCl_2$ and NH_4NO_3 extracting procedures were shown to be appropriate methods for evaluating the mobility of lead in soil, but no informative results were obtained for arsenic. Other extraction methods should be tested for this element.

The addition of amendments promoting plant growth was correlated to the improvement of soil fertility and the reduction of metal(loid) phytotoxicity. This decrease in negative effects due to metal(loid)s could be due to specific chemical linkage between metal(loid)s and soil amendments, and the modification of metal(loid) speciation. These last hypotheses are currently being studied.

In view of the present results, it appears that the best treatment for a field application of an assisted phytostabilization strategy for the technosol of Pontgibaud would be amendments containing either biochar and compost, or biochar associated with slag.

With such combinations of amendments, a better plant growth, a low metal(loid)

translocations in plants, and a decrease in As and Pb concentration in SPW was observed, allowing the threshold limit value for As and Pb to be reached. This will also contribute to stabilizing polluted soils, thus reducing dispersion of metal(loid)s by wind-blown soil transport or mobilization in groundwater. However, it should be noted that the experiments described here were only carried out for a very short time. For these reasons a field test is in progress to observe the effects of the proposed amendments on As and Pb soil stabilization as well as on the capacities of tree growth (*Salicaceae*) in such conditions.

Abbreviations

B, biochar; C, compost; DOC, dissolved organic carbon; EC, electrical conductivity; G, garden soil; ICP-AES, inductively coupled plasma atomic emission spectroscopy; ISO, International Organization for Standardization; Ps, Pontgibaud technosol; S, slag; SPW, soil pore water; TOC, total organic carbon.

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Keywords

amendments, biochar, metal(loid)s, phyto-availability, remediation

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