THE MODIFICATION OF SOIL PROPERTIES AND PLANT UPTAKE BY THE APPLICATION OF BIOEFFECTORS AND AMENDMENTS

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Abstract: *Physico-chemical properties of biomass ashes and biochar were significantly different. Strong differences were also caused by the choice of feedstock materials for incineration, which is demonstrated by different composition and solubility of wood and straw ashes. Availability of nutrients was the highest for K among all tested macronutrients. The application of ash did not adversely affect the growth and yield of plants, neither the accumulation of nutrients in plants and soil. The inoculation of soil by bioeffectors did not affect plant yield but positively influenced the solubility of P. Ash and biochar support sorption and immobilization of toxic metals in soils causing either their lower accumulation in biomass or promoting the growth on the extremely contaminated soil. Both applied materials showed their ability to improve soil properties and support plant growth.*

Keywords: WOOD ASH, STRAW ASH, BIOCHAR, NUTRIENTS, TOXIC METALS, SORPTION

1. Introduction

Soil properties can affect many key parameters in the soil – plant relationship. They can be changed by several ways. Improper soil management, low rates of applied nutrients, as well anthropogenic contamination can negatively affect soil properties and subsequently the rate and quality of crop yield. On the other hand, proper soil management leads to the improvement of soil properties, increasing soil fertility and improving plant growth. Traditional agriculture system was based on the both plant and animal production creating relative stability in soil properties at individual farms. Nowadays, more and more farmers are terminating animal production and are running only crop farms due to globalization, specialization, low price stability of agricultural commodities and dramatic decline of pork meat and milk prices.

This creates new conditions. Manure and slurry, organic fertilizers produced from animal husbandry which stabilized soil properties in large extend in past, are becoming less available causing difficulties in the soil fertility improvement. Lower consumption of crops for animal feeding creates a free space for other plants to be grown or for new utilization of traditional crops on the market. Biomass produced on agricultural land is not only used for food or foodstuff production, but larger areas of land are used for biomass production as a source of renewable energy. Energy accumulated in plant organic matter is mainly transferred into thermal energy producing either heat or electricity and subsequently causing the loss of organic matter and generating a new waste materials originating from soil nutrients, having specific properties and high content of mineral nutrients.

Majority of renewable energy is produced as a heat by the biomass incineration generating ash, the unburned mineral material. In European Union, ash production from biomass incineration reached 5.6 million tones in 2005. The prognosis for 2020 are much higher, up to 15.5 million tones of ash could be produced (Obernberger and Supancic, 2009) as the result of EU agreement to produce 20 % of total energy from renewable resources. Ash is specific waste material, high in pH, rich in several nutrients, but on the other hand, contains some potentially toxic elements and in the case of incomplete burning, containing also some polycyclic aromatic hydrocarbons. Properties of ash also differ according to the type of biomass and technology of incineration. In last decade, several attempts were done to produce energy by biomass pyrolysis as well as to produce biochar, solid undecomposed material, rich in carbon and some other nutrients, having usually alkaline pH and different sorption properties. Due to the origin of biomass, nutrient contents and specific properties, there is a need to bring mentioned materials back to the soil, but only if no adverse environmental effects will be documented. Due to high incineration and pyrolysis temperatures, produced materials are usually very stable in soil.. Therefore, some bioeffectors should be tested in order to modify the release of nutrients from the matrix of mentioned by-products.

The objective of our paper is to show the behavior of different waste materials produced from energy biomass utilization, mainly their effects on soil properties, nutrient release, and plant growth. Additionally, to test the application of bioeffectors, in combination with these materials, in order to change the availability of nutrients in the environment.

2. Results and Discussion

Several experiments were set up to find evidence of ash and biochar application on the soil to affect their properties.

Regarding biomass ash, we can easily recognize two main ashes according to the origin of feedstock material (Table 1). Wood ash has usually higher pH, higher total content of Ca and Mg, but on other hand, its content of all available nutrients is lower. Straw ash is rich in potassium and its solubility is relatively high confirming high nutrient availability. Generally, it can be concluded, that both ashes have a potential to be good sources of less available nutrients, but we have to be very careful, because these materials are significantly different in their composition and solubility. Due to high pH value, both of them can substitute lime for the regulation of soil acidity.

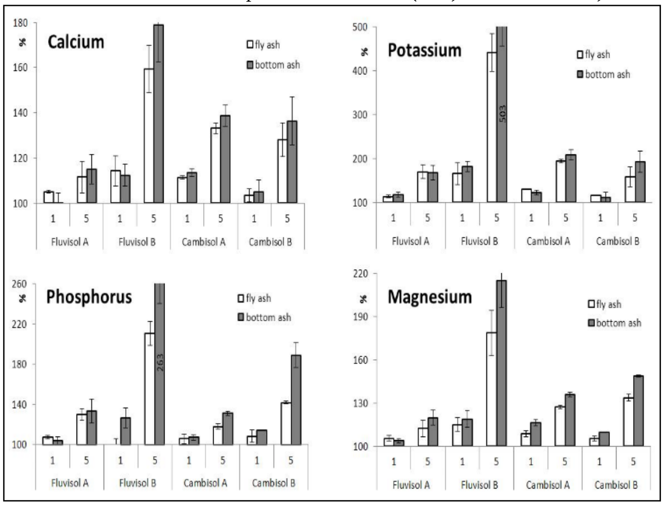
Table 1 *Properties of two ashes of different origin*

Parameters	Straw Ash	Wood Ash
pH_{CaCl2}	10.2 ± 0	11.2 ± 0
pH_{H2O}	10.3 ± 0	11.2 ± 0
CEC (mmol kg^{-1})	261 ± 0.1	125 ± 1.2
Total C (%)	4.8 ± 0.3	8.0 ± 0.7
Total N (%)	0.07 ± 0.01	0.02 ± 0.01
Total CO_3^{2-} (%)	3.13 ± 0.02	4.23 ± 0.18
$Total_{XRF}$ Ca	56 460 ± 160	117 789 ± 200
$Total_{XRF}$ K	159 900 ± 200	58 938 ± 170
$Total_{XRF}$ Mg	9 030 ± 160	17 478 ± 280
$Total_{XRF}$ P	13 610 ± 20	10 195 ± 50
Available Ca_{H20}	354 ± 4	8 208 ± 314
Available K_{H20}	56 037 ± 2 058	3 944 ± 121
Available Mg_{H20}	64 ± 4	23 ± 2
Available P_{H20}	868 ± 20	< 5

Shown values represent arithmetic means ± standard deviation (n = 3).
Pseudototal, total and available portions of Ca, K, Mg and P are given in mg kg^{-1}.

The ash application into a soil can be limited by the presence of potentially toxic elements. If the materials are not contaminated, there is no environmental stress and the contents of toxic metals are relatively low. Contents of metals are also affected by the type of ash. Classical incineration produces mainly bottom ash and about 10 – 20 % of fly ash. Fly ash usually contains significantly higher amount of metals, mainly Cd, which is volatilized at temperatures above 600 ^{o}C and kept there. Fly ash should be properly checked and avoided from soil application.The release of major nutrients was tested at four soils (two Cambisols and two Fluvisols) of different properties. Soils differed in texture (sandy loam – loam), pH (5.0 – 6.1), sorption capacity (low – medium), and nutrient contents (very low – medium). Fly and bottom ashes contained about 10 % of Ca 7 % of K, 1.5 % of Mg and 0.6 % of P. Availability of nutrients fluctuated between 3 and 10 % of total amount and was higher at fly ash for all nutrients. The 56 days incubation of soil and ash mixtures showed higher nutrients availability compared to untreated soil (Figure 1). Availability was higher with the growing rate of ash at all soils and in majority of treatments with bottom ash, which did not correspond to nutrient availability of plain ashes. Higher availability of nutrients from bottom ash could be caused by presence of carbonates in ashes and their solubility in weakly acid soils. The highest nutrient release was found at Fluvisol B for all nutrients, which could be caused by very low sorption capacity of this soil, the lowest one among all tested soils. Among all nutrients, highest release was found for very soluble potassium with no significant differences between bottom and fly ash. Demeyer et al. (2001) also stated that the availability of wood ash derived K was relatively high, and was even similar to mineral K fertilizer.

Figure 1. *The mean relative values of plant available nutrients expressed as a differences from unamended control treatment (100% represents mean control treatment, 1 and 5 represents 1 and 5% (w/w) ash amendment).*



The release of nutrients and the modification of the availability of toxic elements were tested in 3-years pot experiment set up with wood fly ash (WFA), which was applied into two soils with different physicochemical parameters and different levels of risk element contamination. The Fluvisol – (F) light sandy soil from Píšťany area with higher risk element contents (As 51 and Cd 2.6 ppm) and the Cambisol (C) – loamy soil from Příbram contaminated with Cd 4.6, As 70 and Pb 721 ppm. The experiment was set up in six treatments, three on the Cambisol as well as on Fluvisol. Control (0 – I and IV treatments) and annual addition of two ash doses (10 – II and V, 25 – III and VI g/5 kg of soil). Only N was added in annual rate 100 mg N/kg of soil.

Ash pH was high due to the presence of alkaline oxides, we measured value of pH 11.5. The pH values determined in soil samples increased significantly in the case of Cambisol from 5.6 to 7.5 according to the increasing ash dose. For Fluvisol, the pH value increased slightly from 7.1 to 7.3. Similar pattern was observed by Dimitriou et al. (2006), who reported that in all treatments where ash was applied, a higher soil pH than that in the control was observed. Three years cumulative wood fly ash addition (rates up to 1%) into contaminated soils did not negatively affect spring wheat growth.

In wheat, the concentrations of major nutrients (Ca, K, P, Mg) and also Fe and B, predominantly increased with the application of wood ash. Except Mg, grain contents were not significantly influenced by ash application or used soils (Table 2).

Table 2 *Total Ca, K, Mg and P content (mg/kg) in, grains, and straw of spring wheat according to individual treatments*

Grain				
Treatment	**Ca**	**K**	**Mg**	**P**
C-I.	106^{a} (14)	4091^{a} (317)	1261^{a} (194)	4475^{a} (276)
C-II.	115^{a} (12)	4099^{a} (294)	1215^{a} (103)	4251^{a} (426)
C-III.	95,2^{a} (9.7)	4248^{a} (258)	1186^{a} (48)	3867^{a} (289)
F-IV.	159^{a} (23)	4164^{a} (176)	1703^{b} (344)	4938^{a} (266)
F-V.	127^{a} (11)	4113^{a} (169)	1369^{ab} (169)	4265^{a} (344)
F-VI.	116^{a} (15)	4427^{a} (179)	1353^{ab} (94)	4556^{a} (508)
Straw				
Treatment	**Ca**	**K**	**Mg**	**P**
C-I.	2479^{a} (450)	11825^{acd} (944)	1099^{a} (105)	1940^{b} (583)
C-II.	3178^{abc} (552)	12634^{a} (1516)	1074^{a} (51)	1050^{ab} (199)
C-III.	2911^{ab} (467)	12094^{ad} (1116)	1040^{a} (40)	1038^{ab} (248)
F-IV.	4938^{d} (804)	9202,3^{b} (746)	1330^{a} (139)	1382^{ab} (466)
F-V.	4114^{cd} (831)	9897,6^{bc} (666)	1185^{a} (135)	743^{a} (124)
F-VI.	3684^{bc} (730)	10251^{bcd} (669)	1328^{a} (184)	1395^{ab} (464)

Mean values with standard errors in parentheses (n = 9), the values labeled by the same letter did not significantly differ at $p<0.05$.

In terms of soil nutrients (Table3), the significant increase of Ca, K and Mg was observed in both soils after the ash addition. The nutrient availability increased significantly with the elevated dose of ash applied. Available contents of P significantly increased only in Cambisol treatments. Fluvisol was less sensitive to ash addition and values moved around 120 mg P/kg in all three treatments. Available contents of micronutrients in soils were mostly not affected by the ash addition.

Table 3 *Available contents (Mehlich III, mg/kg) of Ca, K, Mg and P in soils after harvest at the end of the experiment according to individual treatments*

Mehlich III				
Treatment	**Ca**	**K**	**Mg**	**P**
C-I.	2040^{a} (14)	120^{ab} (6)	193^{ab} (3)	47.1^{b} (2.2)
C-II.	2212^{a} (68)	137^{b} (4)	206^{b} (2)	52.8^{b} (1.2)
C-III.	2486^{c} (31)	200^{c} (2)	223^{c} (2)	69.4^{c} (1.4)
F-IV.	3300^{b} (13)	79.5^{a} (3.1)	192^{a} (3)	124^{a} (6)
F-V.	3321^{b} (61)	99.2^{ab} (5.6)	200^{ab} (3)	120^{a} (4)
F-VI.	3578^{e} (73)	116^{ab} (2.6)	253^{d} (3)	119^{a} (1)

Mean values with standard errors in parentheses (n = 3), the values labeled by the same letter did not significantly differ at p<0.05.

Fly wood ash and tested soils contained relatively high amounts of toxic elements. We did not observe any detrimental effect for plants after cumulative ash application. Only small amounts of risk elements were taken up by plants. Cd and Pb behaved similarly and their contents in plant decreased with ash addition, in particular at Cambisol treatments (Cd almost by 60 %, Pb by 45 %), Fluvisol treatments were not statistically significant. One of the factors of decreasing risk elements availability in treatments with ash addition was likely pH value increase because of ash alkalinity. Available portions of risk elements in soils determined by Mehlich III extraction (Table 4) showed that As in ash and soils, especially in Cambisol treatments, was tightly bound leading to the availability about 2 % and 3 % of total As. At Fluvisol treatments As availability was negligible. Increased pH value, caused by the ash application, reduced the available Cd in Cambisol treatments while Fluvisol treatments were not affected by the ash possibly due to high buffering capacity of Fluvisol. High Pb amounts in Cambisol treatments corresponded to Pb contamination in original soil. The Pb availability was at the level 35 % and the highest ash dose caused the decrease of Pb by 17 %. Similarly as Cd, Fluvisol treatments were not significantly different and Pb availability was lower (14 %) beside Cambisol treatments.

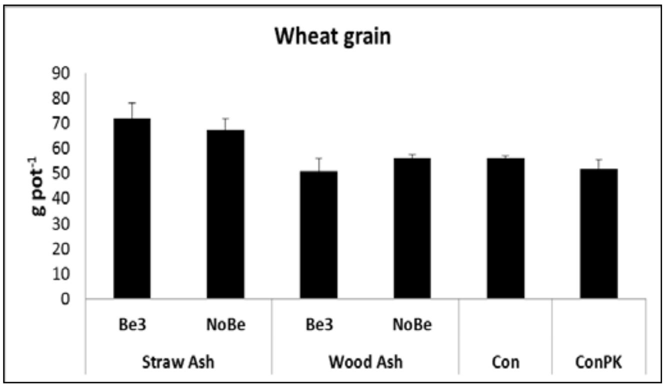
Table 4 *Available contents (Mehlich III, mg/kg) of As, Cd and Pb in soils after harvest at the end of the experiment according to individual treatments*

Mehlich III			
Treatment	**As**	**Cd**	**Pb**
C-I.	1.0^{a} (0.1)	1.6^{c} (0.0)	278^{d} (2)
C-II.	1.1^{ab} (0.1)	1.4^{b} (0.0)	251^{bc} (5)
C-III.	1.6^{abc} (0.1)	1.5^{bc} (0.0)	266^{cd} (3)
F-IV.	1.5^{abc} (0.1)	0.7^{a} (0.0)	14.4^{a} (1.2)
F-V.	1.9^{c} (0.2)	0.7^{a} (0.0)	15.0^{a} (0.4)
F-VI.	1.5^{abc} (0.0)	0.8^{a} (0.0)	15.3^{a} (1.1)

Mean values with standard errors in parentheses (n = 3), the values labeled by the same letter did not significantly differ at p<0.05.

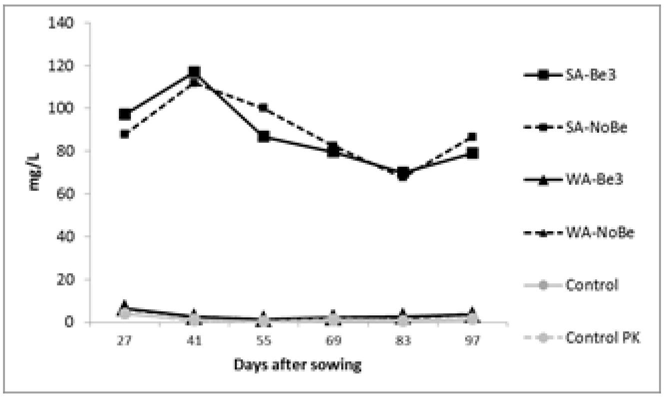
For the improvement of nutrient availability from the ashes, bioeffector was included into pot experiment. Plants of wheat were planted in pots containing 5 kg (d.w.) of soil and 50 g of biomass ash. Soil (Cambisol) and two types of ash (straw –SA, and wood - WA) were tested. Experiment was established in outdoor precipitation-controlled hall. All pots were fertilized by 100 mg N/kg (NH_4NO_3) prior to sowing. Control PK treatments were fertilized by 32 mg P/kg and 88 mg K/kg (K_2HPO_4).

Figure 2 *The yield of wheat grain at treatments with and without straw and wood ash and bioeffector (Be3) application*



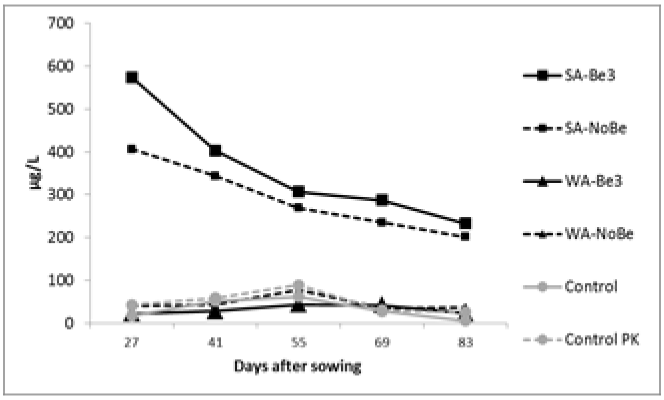
Wheat seeds were inoculated by bioeffector (Be3) twice, firstly at sowing time, secondly in the stage of third leaf development. Be3 treatments were inoculated using 200 ml of RhizoVital® 42 (ABiTEP, Germany) solution (1 ml of RhizoVital ® per L). The yield of wheat grain was positively affected by the application of straw ash only. The higher solubility and higher content of available K in straw ash probably interact with other nutrients and supported the growth of wheat. The inoculation of seeds by bioeffector did not show identical effect at both ashes. Better nutrient availability was at straw ash treatment together with the application of Be3 bioeffector supported growth and showed the best yield among all treatments.

Figure 3 *Potassium content in soil solution at treatments with and without straw, wood ash and bioeffector application during growing period of wheat*



The higher solubility of K in straw ash was confirmed in soil solution (Figure 3). Concentration of K in soil solution treated by straw ash was significantly higher compared to treatment with wood ash, where the soluble K showed similar values to the treatments without ash. The application of Be3 did not changed solubility of K during vegetation period.

Figure 4 *Phosphorus content in soil solution at treatments with and without straw, wood ash and bioeffector application during growing period of wheat*



Straw ash showed also higher solubility of P than wood ash (Figure 4). Concentration of P in soil solution treated by straw ash was significantly higher compared to the treatment with wood ash, where the soluble P showed similar values to treatments without ash. The inoculation of soil by Be3 led to increasing concentration of P in soil solution at straw ash treatment from the beginning of growing period (27 days), where the difference was the highest up to the end of sampling with only small difference. The application of Be3 at wood ash did not show any improvement in phosphorus solubility within five samplings.

The effect of biochar on the changes of soil properties was tested on extremely contaminated soil by Cd 46, Pb 4800, and Zn 4341 ppm. The biochar was derived from coconut shells. The particle size was fraction of 4x2x2mm. Biochar was characterized by: ash content: 12%, pH (in $CaCl_2$): 8.9, CEC: 73mmol$_+$/kg, SSA_{BET}: 486 m^2/g. To observe risk element content in leachate, the lysimeter cylinders were used. The lysimeters were 40 cm tall. At the bottom end, each pot was drained with gravel and placed onto funnel. The leachate was collected into bottle and analysed each 5 weeks during the vegetation. Each lysimeter was filled with 8kg of contaminated soil. *Salix x smithiana* was chosen as an experimental plant. At each treatment, two willows cuttings were planted. The experiment consists of 4 treatments: control (no applied biochar), and rates of 5%, 10%, and 15% of biochar from total mass of soil. Pots were uniquely fertilized with 0.1g N; 0.16g P; 0.4g K per 1kg of soil. Trees were harvested twice, firstly in July, secondly in early October to test maximum accumulation potential of plants.

Figure 5. *Biomass yield of willow leaves and twigs in summer and autumn harvest*

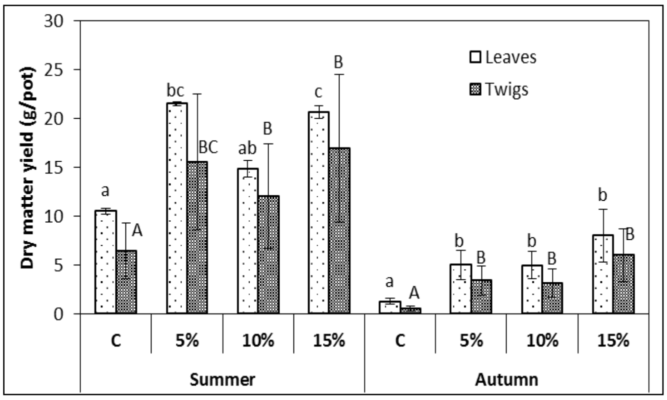
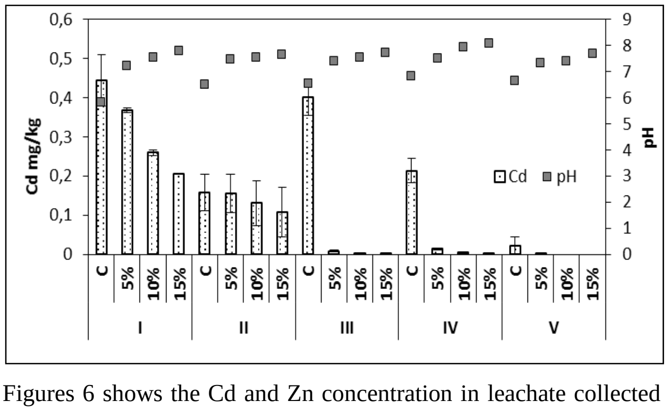


Figure 5 shows the comparison of the willow biomass yield of leaves and twigs separately and evidently the aboveground biomass yield was significantly higher at summer harvest compared to autumn. However, differences among individual treatments were more balanced at autumn harvest. The yield of leaves was higher than twigs at all observed treatments. Significantly lower biomass yield of aboveground biomass was at control at both harvests in comparison to other treatments. With elevating rates of biochar, the yield of aboveground biomass increased. The strong phytotoxic symptoms were observed at control treatment, while biochar showed strong positive effect for the stabilization of mobile contaminants.

Figure 6*. Cadmium content and pH value in leachate collected five times during willow vegetation*



Figures 6 shows the Cd and Zn concentration in leachate collected during willow vegetation. First sampling was after 1 month of growth. There was a visible decrease of Cd concentration in leachate with elevating rate of biochar at first and second sampling. After three months, the reduction of Cd in leachate at biochar treatments was by 97%, 99% and 99% at 5%, 10% and 15% of biochar amended treatments, respectively in comparison to concentrations determined after one month of willow growth. Similarly, Jiang et al. (2012) observed the acid soluble Cd decrease by 86 % after addition of 3 % biochar with no significant difference between 3 % and 5 % of biochar addition. It can be concluded that lower dose of biochar is sufficient stabilization agent. The pH value of leachate increased (in average by 1 unit) with elevating rate of biochar (Figure 6). Leachate from control treatment was slightly acidic and the highest pH value was 8.0 at the treatment with 15% of biochar.

3. Conclusions

Results of presented experiments showed that physicochemical properties of both amendments were significantly different, but pH value, as well as sorption properties and stability of materials were relatively similar. Differences were mainly caused by the completely different structure of ash and biochar. Ash is mainly composed from more or less soluble inorganic salts, while biochar from carbon ring structure. Big difference is also caused by the type of feedstock materials for incineration, which was demonstrated by different composition and solubility of wood and straw ashes. Availability of nutrients in ashes was the highest for K among all tested macronutrients. The application of ash did not negatively affect the growth and yield of spring wheat, accumulation of nutrients in plants as well as in soil increased with the elevated rate of ash. The inoculation of soil by bioeffector did not significantly affect plant yield, but positively influenced the concentration of P in soil solution. Ash and biochar promote immobilization of toxic metals in soils causing either lower accumulation in biomass or promoting growth on the extremely contaminated soil. Both applied materials showed their ability to improve soil properties and support plant growth.

4. Literature

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