Journal Pre-proof

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PII: S0304-3894(20)31133-X

DOI: https://doi.org/10.1016/j.jhazmat.2020.123144

Reference: HAZMAT 123144

To appear in: *Journal of Hazardous Materials*

Received Date: 24 November 2019

Revised Date: 29 April 2020

Accepted Date: 3 June 2020

Please cite this article as: Kończak M, Oleszczuk P, Co-pyrolysis of sewage sludge and biomass in carbon dioxide as a carrier gas affects the total and leachable metals in biochars, *Journal of Hazardous Materials* (2020), doi: https://doi.org/10.1016/j.jhazmat.2020.123144

CO-PYROLYSIS OF SEWAGE SLUDGE AND BIOMASS IN CARBON DIOXIDE AS A CARRIER GAS AFFECTS THE TOTAL AND LEACHABLE METALS IN BIOCHARS

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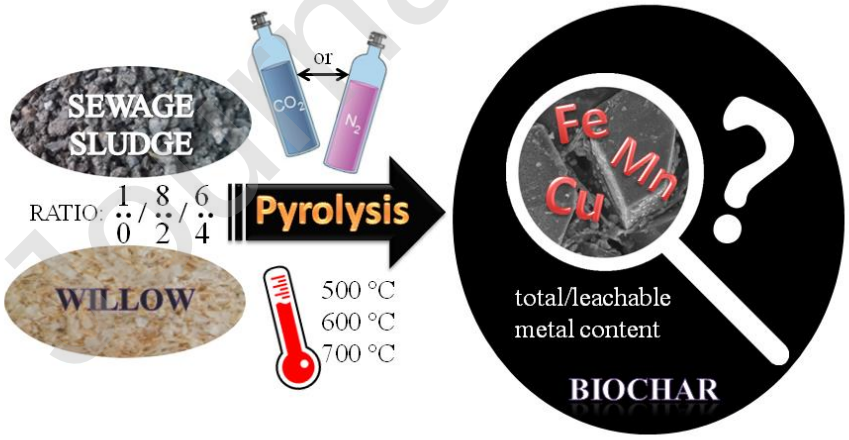
Graphical abstract



Highlights

- Sewage sludge was pyrolyzed with willow to obtain biochar composites
- Biochar was produced in atmosphere of CO_2 as a comparison to N_2
- Total and leachable metals were determined in composites
- Pyrolysis in CO_2 caused the increase the metal content in biochar
- The leachable of metal content depended on carrier gas and dose of biomass

Abstract

The total and available (water extracted) content of selected metal were determined in co-pyrolyzed SSL with willow (8:2, 6:2 w/w) at 500, 600, and 700°C using two different carrier gases (N_2 or CO_2). The study investigated the relationship of metal content and bioavailability to toxicity of biochars towards bacteria (*Vibrio fischeri*), plants (*Lepidium sativum*), and arthropods (*Folsomia candida*).

For the biochar produced at a ratio of 6:4 (SSL:willow), the content of most metals significant decrease ($P \leq 0.05$) from 5.9% to 28.9%. Co-pyrolysis of SSL with willow decreased water extractable metal concentrations (Ba, Cd, Cu, Fe, Mn, Ni, and Zn) from 8.0% to 100%. The CO_2 resulted from 6 to 200% increase ($P \leq 0.05$) of metal content relative to the biochar pyrolyzed in N_2. An increase in pyrolysis temperature caused a higher concentration of the metals in the biochars. The available content of most metals decreased from 9 to 100%. The adverse effect of these biochars on living organisms was reduced due to a stronger binding of the metals (especially Cu and Cd) with the biochar matrix. The negative impact of Cd, Cr, and Cu on living organisms was also confirmed by principal component analysis (PCA).

Keywords: biochar; biomass; gas; metals; sewage sludge; toxicity

1. INTRODUCTION

Sewage sludge (SSL) is a by-product of sewage treatment which also contains, apart from nutrients and organic matter, microorganisms, parasites, and contaminants (heavy metals, polycyclic aromatic hydrocarbons (PAHs), dioxins, furans, pesticides, and more) [1–3]. In recent time, the growing amount of SSL produced has caused the problem related to its economic, but also safe management to become more intense. Currently, each of the known and most frequently applied methods of SSL use/disposal (its use as fertilizer, dumping it into the sea, storage, or incineration) has different drawbacks and is limited by applicable laws. It is very important to seek new methods for safe disposal or management of SSL [4]. One of the directions for the use of SSL is its conversion into biochar that takes place during pyrolysis [5,6]. In the course of pyrolysis, the volume of SSL decreases, parasites are neutralized, while nutrients become more concentrated and can be slowly released to soil [7]. SSL-derived biochar can be successfully used for water and sewage treatment, remediation of degraded areas, or soil amendment [8–11].

Apart from the benefits arising from the conversion of SSL into biochar, one should also note the existing restrictions on its environmental use. During the pyrolysis process, apart from nutrients becoming more concentrated, the content of heavy metals also increases [1,12–14]. The harmful effects of metals present in the SSL-derived biochar on living organisms have been observed [1,15,16]. Heavy metals affected root and shoot growth inhibition and seed germination of wheat (*Triticum aestivum* L.) [16], inhibition of root growth of cress (*Lepidium sativum*) [1,15], inhibition of luminescence of *Vibrio fischeri* bacteria and mortality of *Daphnia magna* crustaceans [1].

A method for reducing metals content can be to add biomass with a lower contaminant load to SSL, which contributes not only to diluting inorganic matter content and toxic compounds present in SSL [3,17], but also to improving other physicochemical properties of produced biochars [3,18,19] and maintaining a high nutrient level. Existing literature information on biochar derived from a mixture of SSL and sawdust or rice straw [17], cotton stems [19–21], and hazelnut [22] or walnut shells [23] proves that in most cases the effect of co-application of SSL and biomass was not only a reduction in total metal content compared to biochar derived from SSL alone, but also the transformation of metals into more stable forms occurred. This phenomenon results in reduced environmental risk from potentially toxic metals during biochar use. Nevertheless, it is worth stressing that existing studies regarding

metal content in biochar produced from a mixture of SSL and biomass without using any additional activators predominantly relate to a ratio of 1:1 [17,19,21]. An exception is a study by Wang et al. [20] where biochar was produced from SSL and cotton stems also at ratios of 1:9, 3:7, 7:3, and 9:1. Unfortunately, this biochar was produced only at one temperature and without comparison with biochar obtained from SSL alone. To explain any effect of biomass on the specific properties, it is necessary not only to change these ratios, but also temperature conditions, and to relate results to biochar obtained from SSL alone. This will be an essential complement to existing research and will allow the existing information gap in this respect to be filled.

Another method that allows the composition of pyrolytic products to be modified is to replace N_2, commonly used as carrier gas [1,6,12], with CO_2 [18,24] during pyrolysis. Our previous study proves that replacement of carrier gas from N_2 to CO_2 during pyrolysis of SSL and biomass results in improved physicochemical properties of biochar produced [18] as well as in a reduced content of polycyclic aromatic hydrocarbons (PAHs) [24] and decrease toxicity of biochars [25]. To date, no research has been undertaken on metal content in biochar produced from SSL and biomass in the presence of CO_2.

The aim of this study was to determine the impact of willow addition to SSL at different weight ratios (8:2, 6:4 w/w) and with use of different carrier gases (N_2 or CO_2) on the total and available metal content in biochar depending on pyrolysis temperature (500, 600, and 700°C). Additionally, the impact of metals present in biochars on their toxicity to various living organisms was evaluated using different statistical tools.

2. MATERIAL AND METHODS

2.1. Determination of heavy metals

Preparation of feedstock pyrolysis and biochar production as well as physico-chemical properties determination of biochar is presented in Internet Supporting Information and in our previous works [18,24]. Biochar digestion was conducted using a START D microwave oven (Milestone, Italy) via a wet method in a mixture of nitric acid (8 mL) and perchloric acid (8 mL) at the ratio of 1:1. A 30% of hydrogen peroxide solution was added before acid. The leachable metal content was determined in leachates obtained according to the EN 12457-2 protocol [26]. The samples were mixed with deionized water in a single-stage batch test performed at a liquid-to-solid (L/S) ratio of 100 g/L. The glass bottles were shaken in a roller-

rotating device at 10 rpm. The extracts were filtered by filter with a porosity of 0.45 μm. Analysis of the Cr, Cu, Ni, Mn, Pb, Cd, Zn, Co, Fe, Ba and Al content was carried out using ICP-OES (Thermo Scientific, ICAP 7000 Series, USA). Evaluation of the accuracy and precision of the analytical procedures used reference materials (Heavy Clay Soil, RTH 953. Promochem).

2.2. Data analysis

In this study, an enrichment factor (EF) was used to assess the influence of pyrolysis conditions on the enrichment of metals in the biochars. The EF was calculated as follows (1):

$$EF = \frac{C_B}{C_M} \quad (1)$$

where C_B is the content of a single metal in the biochars, and C_M is the content of the corresponding metal in the pyrolysis material [20].

Leaching Rate (LR) was used to determining the ratio between of the leachable heavy metal to the total content of each heavy metal. The LR was calculated as follows (2):

$$LR = \frac{C_L * V}{C_T * M} * 100\% \quad (2)$$

were C_L is the concentration of the leachable metal, V is the leachate volume and C_T is the total concentration of metal, M is the raw material mass.

The differences between physicochemical properties and toxicity of biochar and metal content were evaluated using a one-way analysis of variance (ANOVA) followed by Dunnett's post hoc test. Significance was set at $*P \leq 0.05$. Principle component analysis (PCA) was carried out with metal content and toxicity of all biochars based on the correlation matrix method, using Statistica.

3. RESULTS AND DISCUSSION

3.1 Total and extractable metals in SSL-derived biochar

The content of the metals in the biochars produced from SSL and from SSL/willow mixture in an atmosphere of N_2 was strictly determined by their content in the feedstock (Table S1). Depending on pyrolysis temperature, the metal content in biochar did not change relative to the feedstock or increased (1.7 times at the maximum). In most cases, the enrichment factor (EF) for the studied biochars ranged from 1.03 to 1.71 (Table 2). An increase of metals after pyrolysis in biochar is a common phenomenon [1,14] and is associated with transformation of

a large part of the feedstock. Metals in SSL most frequently occur as mineral salts (chlorates, carbonates, sulfates, phosphates), sulfides, hydroxides, and oxides, which are transformed predominantly into compounds with higher thermostability during pyrolysis [27]. Due to this, most metals present in SSL become more concentrated [1]. An exception was Al, which decreased in comparison with SSL (Table 2). It suggests that this metal exhibits a tendency to volatilize and migrate during pyrolysis.

Metal content in the SSL-derived biochar varied and depended on the type of element and pyrolysis temperature (Figure 1-2, Table S1). With increasing pyrolysis temperature, Al, B, Ba, Cd, Cr, Cu, Fe, and Mn content was observed to increase, which in most cases was associated with mass losses during pyrolysis. This phenomenon is confirmed by the statistically significant correlations ($P \leq 0.05$) between Al, Ba, Cd, Cr, and Mn and yield (Table S2). For Co, Ni, Pb, and Zn, their content increased to 600ºC, while at 700ºC decreased. The reduced level of some metals, particularly at high temperatures, can indicate partial defractionation and/or partial volatility of these elements at elevated temperatures [1,28]. A similar phenomenon at 700ºC was observed by Hossain et al. [28] where the content of Cr, Ni, and Pb decreased during SSL pyrolysis.

The metal content found in the studied biochars was lower than the content observed for other SSL-derived biochars [1,27,29]. This results from a low level of metal contamination of SSL used in present study (Table S1). In spite of this, the content of Cd, Cr, Cu, Ni, Pb, and Zn, for which the permissible levels in biochar are estimated in Germany's Federal Soil Protection Act and Switzerland's Chemical Risk Reduction Act [30], exceeded the standard limits. The Cr and Pb content were only below the permissible levels (Figure 1).

The concentrations of most of the metals in leachates were low and ranged from 0.01 to 1 mg/L. It is evident that metals contained in biochar will be immobilized after their application to soil, which reduces soil contamination and accumulation of metals in living organisms. In the present study, in most cases the contents of available metals in the SSL-derived biochar were lower than those noted by other authors who used various extraction reagents [27,29]. For example, in SSL-derived biochar, Chen et al. [29] found several hundred times higher content of available Cd, Ba, Cu, Ni, Pb, and Zn after extraction by mixture of sulfuric acid and nitric acid. Using DI-water, $CaCl_2$, EDTA, CH_3COOH, and NH_4NO_3, Farrell et al. [31] also observed the diverse range of metals leaching from biochars. Due to the fact that various methods have been applied [29,29,31] in evaluation of the availability of metals in biochar and there are no official recommendations, the selection of an optimal extraction reagent is more difficult. Water is a relatively mild solvent but seems to be a good predictor of

immediate risk of metals being leached from biochar due to of natural factors (e.g. rainfall, surface runoff, etc.).

Pyrolysis temperature did not regulate Cd, Co, Cr, Cu, Fe, Ni, and Pb leaching from the SSL-derived biochars, which had been previously documented by Lu et al. [27]. It is accepted that during pyrolysis a temperature of 400°C is sufficient to stabilize metals [27]. Hence, application of elevated temperatures does not usually cause significant changes in the content of metals leached from biochar [27]. The only exceptions were Ba (with increasing pyrolysis temperature, its concentration in the biochar was observed to increase) as well as Al, B, Mn, and Zn (with increasing pyrolysis temperature, their concentration in the biochar was observed to decrease).

The determined leaching rates (LR) (Equation 2) for the biochars (Table 4) were lower than those obtained for SSL. This is evidence that during pyrolysis a large part of mobile metals are transformed into more stable forms, which are meagerly soluble and difficult to leach [27,29]. The lower release of metals from biochar than from SSL results from a more developed structure of biochar pores, a larger specific surface area of biochar, and functional groups (metalo-organic complexes) formed on the biochar surface during pyrolysis [13,27,32].

3.2. Impact of CO_2 on total and extractable metals in SSL-derived biochar

Significant differences ($P \leq 0.05$) were observed in metal content in the biochar depending on the carrier gas used (Table S1, Figure 1-2). For most of the metals, their content in the biochars produced in CO_2 was higher from 7.8% to 200% ($P \leq 0.05$) than during pyrolysis in N_2. The use of CO_2 instead of N_2 had the highest impact on Al (from 180 to 211%) and B (from 10.3 to 43%), while the lowest impact on Cr (from 7.8 to 10.0% only at 600 and 700°C) and Zn (from 7.9 to 16.0% only at 600 and 700°C). Compared to the biochars produced in an atmosphere of N_2, no statistically significant changes ($P \leq 0.05$) were found at 500°C for Zn, Ni, Pb, Cr, Mn, and Fe. At the other temperatures, however, a significant increase ($P \leq 0.05$) in the content of these metals was observed after application of CO_2 compared to N_2. The increased concentration of the metals observed many times for biochars produced in CO_2 resulted from the higher feedstock mass loss during pyrolysis in an atmosphere of CO_2 than for N_2 (Table 1). Feedstock loss increased with increasing pyrolysis temperature, which aggravated the effect of elevated concentration of most of the metals. This assumption is

confirmed by the statistically significant negative correlations ($P \leq 0.05$) between metal content and pyrolysis yield (Table S2) as well as a higher enrichment factor (EF) was obtained (Table 2) for the individual metals identified in the biochar produced in an atmosphere of CO_2 relative to N_2.

The change of carrier gas also had an impact on the content of water extractable metals (Table 2). Compared to the biochars produced in N_2, the biochars obtained in CO_2 were characterized by a lower content of the available fraction from 16.0 to 100%. Furthermore, Cd, Co, and Pb content were below the detection limit in the biochars produced in CO_2. It was only in the case of Al that even more than twice higher values were recorded for the biochars produced in CO_2 than in N_2. For Al, Cu, Fe, Mn, and Zn, an increase in pyrolysis temperature, in particular to 700°C, additionally had an effect on reducing the amount of extractable metals.

The reduction in the level of available metals was associated with the development of the biochar physicochemical properties as affected by the CO_2, which were different than those in an N_2 atmosphere. The biochars produced in CO_2 were characterized by a higher number of different functional groups occurring on the biochar surface than N_2, which was confirmed by more intensive bands in the dactyloscopic region of the FT-IR/PAS spectra - below 1500 cm^{-1} (for instance, the bands of ~1400 cm^{-1} and ~1100 cm^{-1}) [33] (Figure S1). The surface of the biochar produced in the presence of CO_2, more carbonized (Table 1) and richer in functional groups, could have caused an increase in the degree of immobilization of the metals in the biochar as a result of their being additionally trapped [19]. A confirmation of the transformation of the metals into more stable forms during the pyrolysis process is also the lower LR than in the biochars produced in an N_2 (Table 4). An exception was the previously mentioned Al. The obtained results for Al content and LR are evidence that during pyrolysis in a CO_2 this element undergoes transformations contributing to reducing its mobility to a lesser extent in comparison to the other metals.

3.3 Impact of biomass on total and extractable metals in SSL-derived biochar

Willow addition to SSL depending on temperature and rate used had a varying effect on metal content in biochars. Willow added at a rate of 20% to SSL (a 8:2 ratio) did not affect significantly ($P \leq 0.05$) B, Cr, Cu, and Zn content in the biochar (Figure 1 A, B, D; Figure 2 E). For Ni and Co (only at 700°C) (Figure 1 E, Figure 2 A), Pb, Mn, Fe, and Ba (at 600 and

700°C) as well as Cd and Al (at 500, 600, and 700°C) (Figure 1 F, Figure 2 B, C, D), an increase in their content ranging from 6.2 to 45.3% was found.

Co-pyrolysis of SSL and willow at a ratio of 6:4 usually caused a decrease in metal content in the biochar compared to the SSL-derived biochar (Figure 1, Figure 2). Regardless of pyrolysis temperature, a decrease in Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn content was found to range from 5.9% to 28.9%. The highest reduction was observed for Pb (from 16.1 to 28.9%), Ni (from 10.0 to 28.7%), and Zn (from 15.0 to 19%), while the lowest one for Cu (from 6.0 to 7.6%) and Mn (from 5.9 to 10.1%). The reduction relative to the biochar derived from SSL alone was usually highest in the biochars produced at a temperature of 500°C, whereas the lowest one at 700°C, which correlated with the pyrolysis yield changes (Table 1). Observed reduction of metals content in biochar produced with SSL and willow (6:4) can be explained in two ways: (1) The addition of willow to SSL reduced the total metal content due to the "dilution effect" or (2) During pyrolysis, due to changes in the composition of the raw material, some metals (especially those with low boiling points such as Cd, Zn, and Pb) were reduced to single metals under anaerobic conditions and were transferred into the gas phase or bio-oil [20]. The reduction in metal content in co-pyrolyzed biochar (6:4) contributed to meeting the criteria for the standard concerning Ni (Figure 1 E), as determined by Germany's Federal Soil Protection Act and Switzerland's Chemical Risk Reduction Act [30], and for Cd (Figure 1 C) presented in Germany's Federal Soil Protection Act [30]. Thus, an appropriate addition of biomass to SSL can enable the potential possibility of SSL management to increase by both the adjustment of the level of contaminants to the applicable standards and a reduction in risk arising from the presence of metals as a result of biochar application to soils.

For Ba and B, no statistically significant differences ($P \leq 0.05$) were found between their content in the biochar obtained from a mixture of SSL and willow at a ratio of 6:4 and the biochar from SSL alone, whereas the Al and Fe content increased respectively from 127.0 to 169.0% and from 10.2 to 12.7%.

The effect and importance of the rate of biomass addition to SSL on metal content in biochar was previously investigated by Wang et al. [20]. These authors did not observe 10 and 30% rates of biomass addition to SSL to have a significant effect ($P \leq 0.05$) on Cd, Cr, and Pb content in biochar produced. A decrease in the content of all metals analyzed was observed only at a 50% biomass addition compared to lower biomass addition rates [20]. Nevertheless, this study lacked a comparison of co-pyrolyzed biochars and SSL-derived biochars, which would be helpful in interpreting the results and explaining any differences. In turn, a reduction

in metal content in biochar derived from biomass and SSL (1:1) compared to biochar from SSL alone was observed by Huang et al. [17] and Jin et al. [19]. Co-application of biomass and SSL can be an effective method for reducing metal content in biochar. To achieve the intended effect, however, it is important to ensure an appropriate proportion of biomass in SSL, which should be at least 40% according to our research, obviously depending on the degree of biomass contamination by metals.

Regardless of the proportion of willow, co-pyrolysis of SSL and willow decreased the available content of Ba, Cd, Cu, Fe, Mn, Ni, and Zn from 8.0% to 100% relative to the biochar derived from SSL alone (Table 3). For B, Co, and Pb, there was a statistically significant decrease ($P \leq 0.05$) in their available content only for a SSL/biomass ratio of 6:4. On the other hand, no change was observed for Al and Cr irrespective of the willow addition rate used. Reduced release of the metals from the biochars after adding biomass to SSL was probably caused by a different transformation of the chemical forms of the metals during the process of co-pyrolysis of SSL and willow relative to SSL alone. Conversion of metals into more stable occluded forms after adding biomass (bamboo sawdust) to SSL was observed by Jin et al. [19]. Transformations of metal forms are associated with chelation by new functional groups formed due to the presence of biomass. The interaction between metals present in SSL and inorganic minerals from biomass and SSL during the pyrolysis process, may lead to occlusion of some metals in minerals like feldspar or quartz also occurs [19,23]. In our research, the lack of additional peaks in the FTIR spectrum of biochar from SSL and willow compared to biochar from SSL alone (Fig. S1 A, C) excludes a significant effect of functional groups on increasing the mobility reduction of metals present in biochar. Occlude the metal ions in the lattice of crystalline structures of silicate minerals is more possible. The presence of quartz and other inorganic mineral compounds in biochar obtained from SSL and willow is confirmed by XRD (Table S3) and band analysis on FTIR spectra (538 cm^{-1}; Al-O-Si and 1035 cm^{-1}; Si-O-T; T-tetrahedral Si or Al unit) [33,34] (Fig. S1 C). Release of heavy metals from biochar is also reduced through additional development of the specific surface area as a result of the presence of biomass [17], which also occurred in our study (Table 1). An increase in biochar S_{BET} after adding willow to SSL is a result of the removal of volatile substances from biomass during pyrolysis, in effect forming a more porous materials than that obtained in the case of SSL alone [24,35]. The statistically significant relationships ($P \leq 0.05$) between S_{BET} and Co, Cd, Fe, and Mn content confirm the key role of this parameter in reducing the availability of these metals (Table S4). Biochar obtained from SSL and willow were characterized by lower H/C, O/C and (O + N)/C molar ratios when compared to biochar

from SSL alone (Table 1), which indicates the increase in aromatization, carbonization and the decrease in hydrophilic character of biochar surfaces. A molar H/C ratio ⩽0.3 generally indicates highly condensed aromatic ring systems [19]. Therefore, the aromatic compounds can supply π-electron and have a strong ability to bond metal cations, and thus reduce the release of metals [34,36].

Wang et al. [20] observed that the degree of metal leaching from biochar, apart from the presence of biomass itself, is also affected by its quantity. An increasing proportion of biomass in SSL during pyrolysis results in enhanced transformations of metals from mobile fractions to those more stable ones, which indicates a reduction in potential environmental risk associated with the presence of metals in biochar. This phenomenon is also confirmed by the decreasing LR values with increasing willow rates which were obtained in our study (Table 4).

To sum up, it can be concluded that the immobilization mechanism of metals by biochar produced with SSL and willow compared to biochar from SSL alone was probably based on: (1) metal entrapment in the pores of the biochar matrix, (2) metal occlusion in minerals, (3) π-bonding with electron rich domains on aromatic structure. The mechanisms are shown in Figure S2.

3.4 Impact of CO_2 on total and extractable metals in co-pyrolysed biochar

Co-pyrolysis of SSL and willow in a CO_2 atmosphere also had an impact on metal content in the biochar. In comparison with the biochars produced in an N_2 atmosphere, for Al, B, Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn an increase in their content was noted (from 6.0 to 93.7%). The highest enrichment rate was found for Al (from 62.4 to 93.7%), Pb (from 9.3 to 35.0%), and Co (from 15.4 to 29.5%), whereas the lowest one for B (from 6.0 to 8.6%). No statistically significant changes ($P \leq 0.05$) were observed only for Ba and Fe. The observed increase in metal content in the biochars, similarly to the biochars from SSL alone, was probably caused by the increased mass loss during the pyrolysis process in the presence of CO_2 compared to N_2 (Table 1, Table S2), which was widely discussed earlier. The obtained results allow to speculate that the CO_2 atmosphere may significantly inhibit the "dilution effect" after adding willow to SSL and decrease the loss of metals through their volatilization.

Application of CO_2 as carrier gas instead of N_2 with respect to the co-pyrolyzed biochars also affected the available metal content in the biochars produced. In spite of an increase in total metal content, in most cases the available metal content was observed to decrease from 9.0 to

100%. Co, Pb, and Cd were not identified in these biochars (Table 3), which indicates a complete binding of these metals in less-available and unavailable forms. The lack of significant differences in the degree of aromatization (Table 1), type of functional groups (Fig. S1 C, D) and mineral composition (Table S3) of biochar obtained in the atmosphere of CO_2 compared to N_2 suggests that the main mechanism responsible for more effective reduction of metal mobility is probably entrapment in the pores due to more developed biochar specific surface area (Table 1) [13,27,32] (Fig. S2). However, it should be noted that the other processes affecting the immobilization of metals mentioned above (occluded in minerals and π-bonding with electron rich domains on aromatic structure) are still present but have similar intensity and thus don't increase the effect of metal immobilization. The lower LR value obtained in the co-pyrolyzed biochars produced in a CO_2 atmosphere compared to that found for the same biochars produced in N_2 (Table 4) confirm that limited release of the metals was due to their more effective transformations into less available forms of the produced biochars (Table 1). Similarly as in the case of the biochars derived from SSL alone, Al was an exception because in this case a several-fold increase in its content was noted and higher LR rates were found than for the biochars produced in the presence of N_2 (Table 4). This confirms that during pyrolysis in the presence of CO_2, compared to the biochars produced in an atmosphere of N_2, different transformations of Al forms occurred than for other metals studied, which consisted in the formation of more mobile forms.

3.5. Relationship between metal content and toxicity of biochars

Contamination of the environment with metals is one of the main hazards that can cause improper functioning of living organisms. Therefore, it is very important to determine the impact of metals present in biochar – which is often used as a soil amendment – in relation to representatives of various trophic groups. To estimate the effect of willow addition and carrier gases (N_2 or CO_2) on the toxicity of the produced biochars due to the presence of the metals in question, a statistical analysis was performed (Table S5 and Table S6). Detailed results of bioassays are included in SI (Figure S3-S4).

The obtained positive correlations (Table S5-S6) between Cu and Cd content (total and available) in the SSL-derived biochar ($P \leq 0.05$) and toxic effect on plants can indicate a negative impact of these metals on the growth and development of the test plants. A previous study [37] confirmed that the presence of Cd in soil can disturb photosynthesis and influence changes in cell membrane permeability, while Cu can cause disturbances in root growth in

plants. In turn, the adverse impact of the SSL-derived biochar on arthropods – *F. candida* – could also have been associated with the presence of Cd ($P \leq 0.05$) in the soil solution (Table S5). Cd can contribute to the inhibition of reproduction and body growth in arthropods [38]. For *V. fischeri*, the metals present in the biochar extracts were not found to have a significant impact on these microorganisms.

Despite that the total content of some of the metals increased in the produced biochars (Figure 1-2), neither willow addition nor the change of carrier gas from N_2 to CO_2 caused the negative impact of the biochars on the test organisms to increase (Figure S3-S4). This allows us to assume that the form of metal (total, available) has an important role in determining biochar toxicity. The absence of statistically significant relationships between the content of available metals in the biochar produced from SSL in a CO_2 atmosphere or in the co-pyrolyzed biochars in the presence of N_2 or CO_2 and toxic effect is evidence of the reduced degree of adverse impact of the metals present in the biochar derived from SSL alone in the presence of N_2 on living organisms. This was associated with the transformation of the metals during pyrolysis of SSL with the addition of willow or in the presence of CO_2 into more stable/less easily available or unavailable forms, which resulted in a reduced amount of mobile forms of the metals, which could actually affect negatively the living organisms.

To obtain more in-depth information on the effect of the metals present in the biochar on their toxicity, a principal component analysis (PCA) was performed (Figure 3). Depending on bioassay and biochar rate applied, in solid phase assays the biological responses of the test organisms were most strongly positively correlated with metals such as Al, B, Cd, Cr, and Cu (Figure 3A). In the case of the available metal content, the highest relationships were observed for Cd (Figure 3B). The obtained PCA results are largely in agreement with Pearson's correlations derived for the biochars produced from SSL in an atmosphere of N_2 (Table S5 and Table S6). This allows us to presume that the content of metals such as Cd, Cr, and Cu in the biochar mostly affected its toxicity.

4. CONCLUSION

Co-pyrolysis of SSL and biomass (willow) can be one of effective methods for reducing mobility and toxicity of metals in biochar. Nonetheless, an appropriate proportion of willow in SSL during pyrolysis is important since too low a proportion of biomass can reduce the "dilution effect". It should however be stressed that at a lower biomass to SSL ratio, the effect

of reduction of the available fraction of metals was also significant. Nevertheless, with increasing temperature the metals in the biochar were concentrated more strongly, which was a result of the increased mass loss during co-pyrolysis. In the biochars produced in the presence of CO_2, there was also stronger immobilization of the metals in the biochar compared to N_2. Unfortunately, the use of CO_2 during pyrolysis adversely influenced total metal content. It is particularly important in relation to the standards that are determined based on total metal content.

Credit Author Statement

Magdalena Kończak (Conceptualization) (Methodology) (Investigation) (Writing - original draft), Patryk Oleszczuk (Conceptualization) (Review and editing) (Supervision)

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The project (2018/30/Q/ST10/00060) was funded by the National Science Centre.

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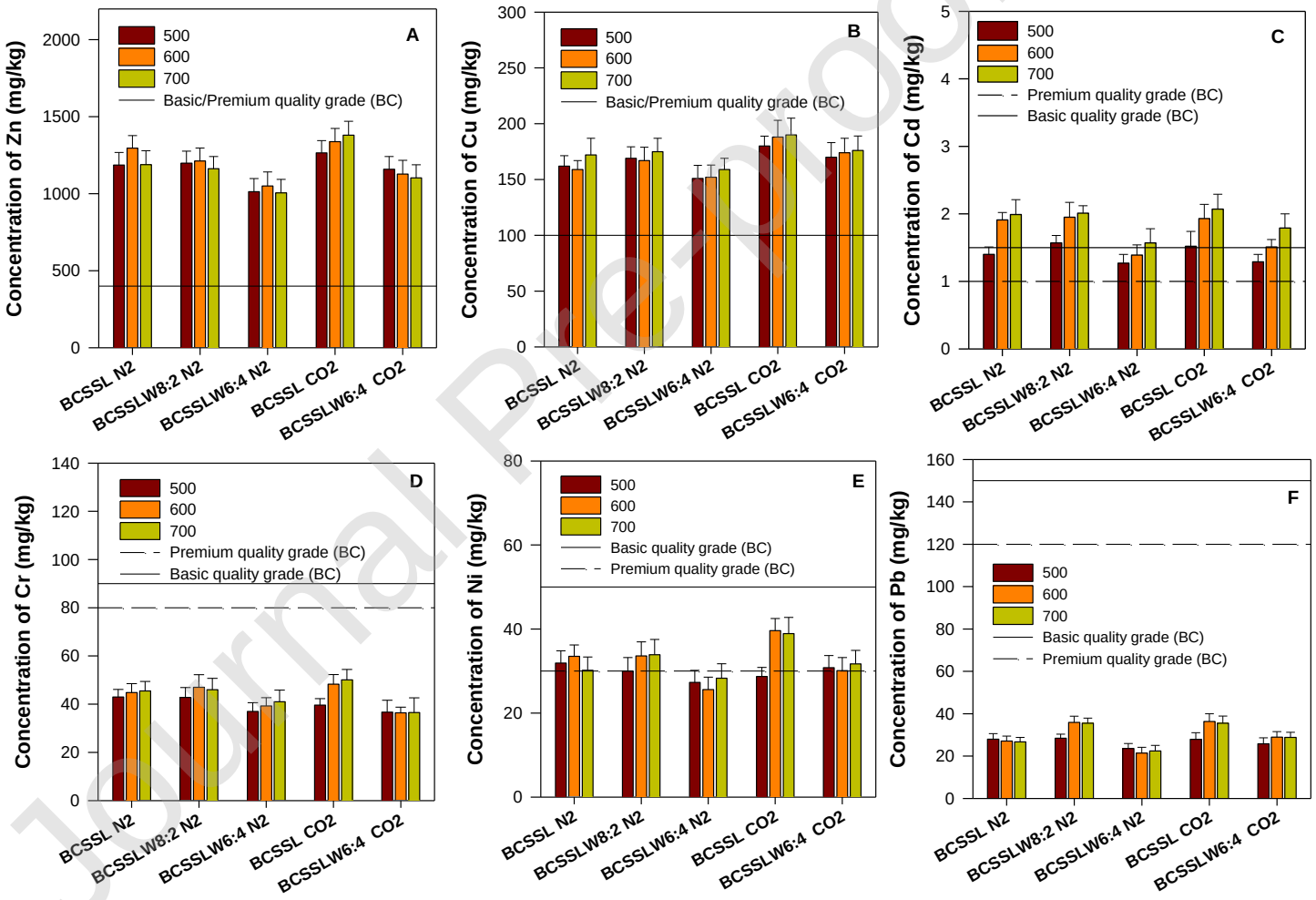

Figure 1. Metal content (mg/kg) in biochar produced from SSL (BCSSL) or SSL and willow (BCSSLW8:2, BCSSLW6:4) at different temperature (500, 600, 700°C) and carrier gases (N_2 or CO_2). Values are given as averages with standard deviations (n = 3). The metal content to compared with the threshold concentrations according to Germany's Federal Soil Protection Act (basic quality grade biochar) or Switzerland's Chemical Risk Reduction Act (premium quality grade biochar) [30].

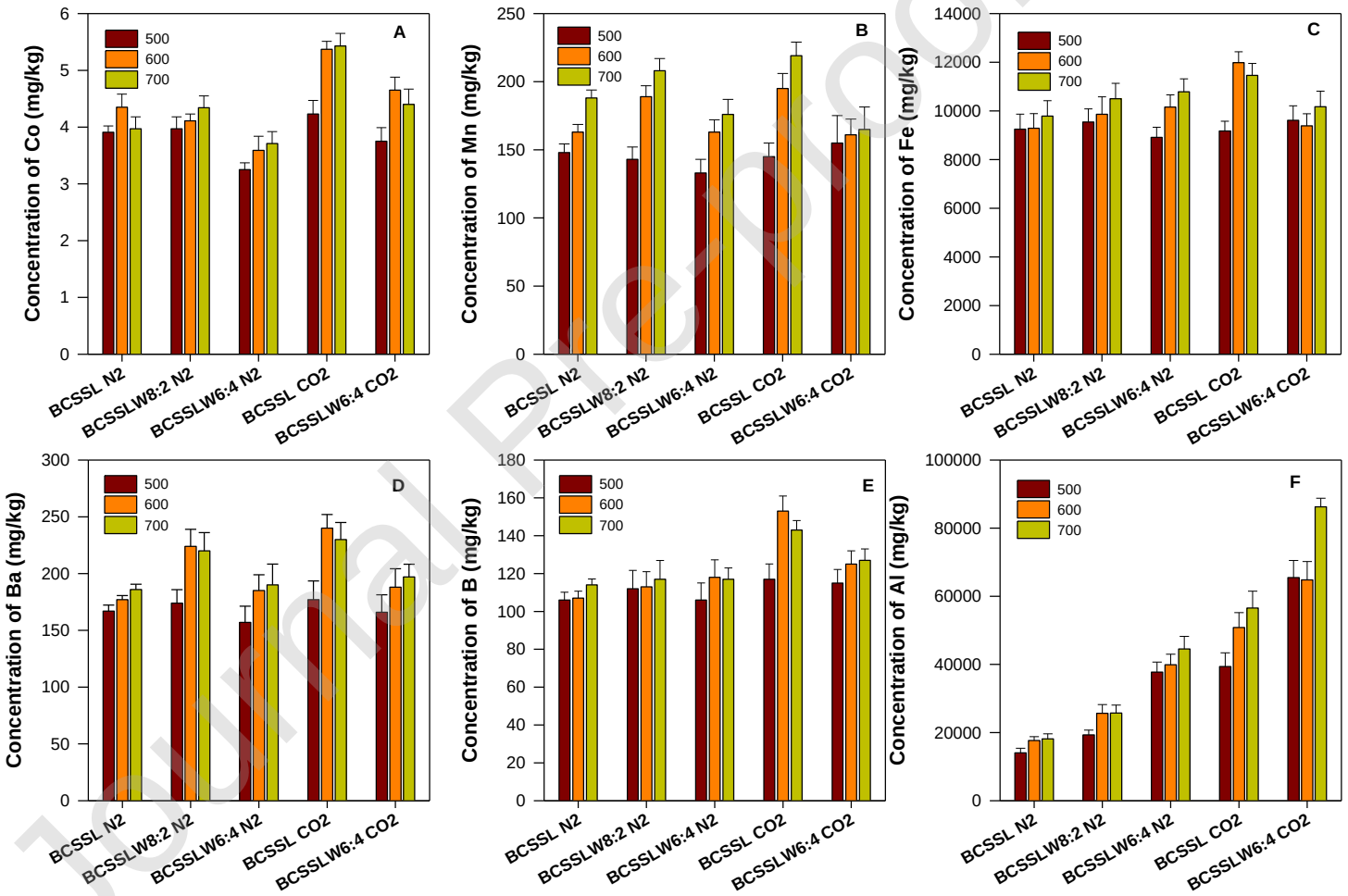

Figure 2. Metal content (mg/kg) in biochar produced from SSL (BCSSL) or SSL and willow (BCSSLW8:2, BCSSLW6:4) at different temperature (500, 600, 700°C) and carrier gases (N_2 or CO_2). Values are given as averages with standard deviations (n = 3). The threshold concentrations of this metals in biochar they were not specified in European biochar certificate - guidelines for a sustainable production of biochar [30].

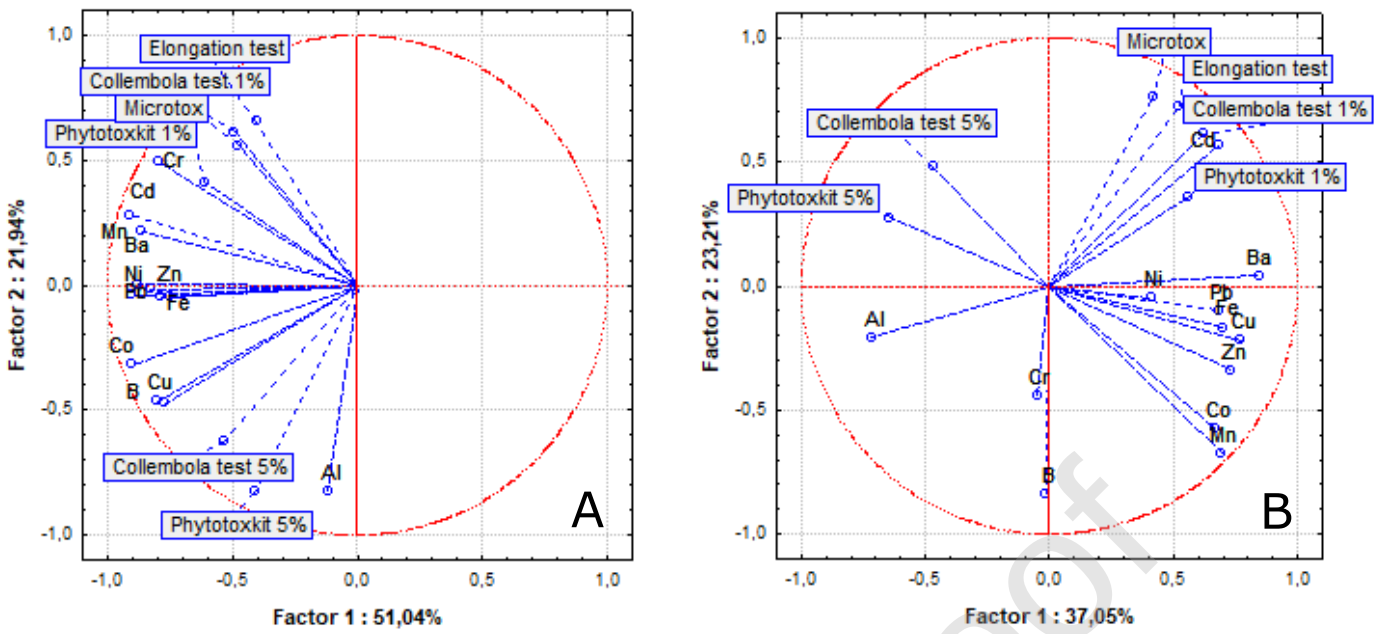

Figure 3. Principal component analyses (PCA) relating the toxic endpoints to total (A) and leachable (B) metal content.

Table 1. Properties of sewage sludge-derived biochar (BCSSL) and co-pyrolysed sewage sludge with willow (BCSSLW8:4, BCSSLW6:4) at various temperatures (500-700ºC) and different gases (N_2 and CO_2).

BC	Temp. pyrolysis (°C)	GAS	pH	EC	C	O/C	H/C	(O + N)/C	TOC	DOC	N	S_{BET}	PY
BCSSL	500	N_2	9.4	2.3	26.3	0.15	0.45	0.26	26.2	19.6	3.26	69.7	51.0
BCSSL	600		12.1	4.8	26.5	0.07	0.27	0.16	26.4	11.9	2.93	75.5	46.6
BCSSL	700		12.4	9.0	24.5	0.05	0.19	0.13	24.4	9.7	2.10	89.2	44.4
BCSSLW8:2	500		10.7	2.2	34.3	0.10	0.39	0.19	33.8	15.8	3.41	75.3	44.3
BCSSLW8:2	600		12.1	4.7	35.8	0.02	0.22	0.10	35.3	12.2	3.08	88.4	43.4
BCSSLW8:2	700		12.5	8.2	32.6	0.03	0.16	0.08	32.2	9.9	2.24	99.0	40.2
BCSSLW6:4	500		10.8	1.7	44.6	0.07	0.34	0.13	44.2	16.6	3.33	74.6	40.8
BCSSLW6:4	600		12.1	4.4	45.2	0.03	0.21	0.08	44.9	12.5	2.85	93.1	39.2
BCSSLW6:4	700		12.5	8.5	46.2	0.02	0.16	0.04	46.0	9.0	2.09	104.1	36.2
BCSSL	500	CO_2	9.2	2.5	25.1	0.35	0.32	0.46	24.5	17.8	3.17	71.1	48.0
BCSSL	600		9.5	1.7	25.5	0.21	0.18	0.30	24.9	10.2	2.82	74.7	43.3
BCSSL	700		9.8	1.1	22.7	0.10	0.09	0.17	22.1	6.6	1.86	83.5	40.3
BCSSLW6:4	500		9.3	1.9	44.7	0.12	0.32	0.18	44.2	22.3	3.35	88.7	42.1
BCSSLW6:4	600		9.5	1.5	51.1	0.01	0.24	0.05	50.5	11.2	2.58	114.8	35.2
BCSSLW6:4	700		9.8	1.0	47.7	0.01	0.15	0.06	47.2	11.7	2.49	152.5	33.3

pH- in H_2O; EC- electrical conductivity (mS cm^{-1}); C, N - carbon. nitrogen total content (%); O/C, H/C, (O+N)/C - molar ratios; TOC – total organic carbon (%); DOC – dissolved organic carbon (mg L^{-1}); S_{BET}- specific surface area of adsorbents (m^2 g^{-1}); PY (%)- pyrolysis yield; The values are mean of three repetitions

Table 2. The values of enrichment factors (EF) of metals in the sewage sludge-derived biochar (BCSSL) and co-pyrolysed sewage sludge with willow (BCSSLW8:4, BCSSLW6:4) at various temperatures (500-700ºC) and different gases (N_2 and CO_2).

Biochars	Gas	Zn	Cu	Cr	Ni	Cd	Pb	Co	Mn	Fe	Ba	B	Al
BCSSL500		1.23	1.03	1.05	1.16	1.23	1.22	1.08	1.22	1.23	1.11	1.05	0.26
BCSSL600		1.24	1.01	1.09	1.15	1.68	1.18	1.07	1.35	1.23	1.18	1.06	0.32
BCSSL700		1.23	1.09	1.11	1.10	1.71	1.17	1.10	1.55	1.30	1.24	1.13	0.33
BCSSLW8:2 500		1.38	1.22	1.19	1.43	1.57	1.42	1.37	1.30	1.41	1.27	1.23	0.37
BCSSLW8:2 600	N_2	1.39	1.20	1.31	1.60	2.11	1.80	1.42	1.72	1.45	1.64	1.24	0.49
BCSSLW8:2 700		1.34	1.27	1.28	1.61	2.21	1.78	1.50	1.89	1.55	1.61	1.29	0.49
BCSSLW6:4 500		2.74	2.80	3.03	2.78	2.82	2.37	2.64	2.63	1.57	1.50	1.24	0.76
BCSSLW6:4 600		2.84	2.80	3.22	2.50	3.09	2.15	2.92	3.23	1.85	1.76	1.38	0.81
BCSSLW6:4 700		2.72	2.93	3.36	2.98	3.49	2.25	3.02	3.49	1.91	1.81	1.40	0.90
BCSSL500		1.24	1.14	0.96	1.05	1.33	1.22	1.17	1.20	1.22	1.18	1.16	0.72
BCSSL600		1.38	1.19	1.18	1.45	1.84	1.59	1.49	1.61	1.59	1.60	1.51	0.93
BCSSL700		1.43	1.20	1.22	1.42	2.08	1.55	1.50	1.81	1.52	1.53	1.42	1.03
BCSSLW6:4 500	CO_2	3.13	3.13	3.01	3.13	2.87	2.59	3.05	3.07	1.70	1.58	1.34	1.33
BCSSLW6:4 600		3.05	3.20	2.98	3.06	3.36	2.90	3.78	3.19	1.87	1.79	1.46	1.31
BCSSLW6:4 700		2.98	3.24	2.99	3.22	3.98	2.89	3.58	3.27	1.93	1.88	1.48	1.75

Table 3. The content of water extractable metals (mg/L) in feedstock and biochars pyrolysed at different temperature (500, 600 and 700°C) and N_2 or CO_2 atmosphere.

Sample	GAS	Zn	Cu	Cr	Ni	Cd	Pb	Co	Mn	Fe	Ba	B	Al
SSL	-	10.97 ± 0.51	0.73 ± 0.02	0.12 ± 0.02	2.39 ± 0.3	0.26 ± 0.002	0.31 ± 0.01	0.48 ± 0.02	8.47 ± 0.52	22.3 ± 1.90	1.02 ± 0.20	22.3 ± 1.30	1196 ± 59.3
W		5.24 ± 0.22	0.27 ± 0.03	0.04 ± 0.001	0.23 ± 0.01	0.01 ± 0.001	0.10 ± 0.02	0.01 ± 0.002	1.96 ± 0.20	3.35 ± 0.41	0.41 ± 0.02	0.41 ± 0.01	134 ± 12.3
SSL:W8:2		8.61 ± 0.45	0.53 ± 0.01	0.09 ± 0.003	1.79 ± 0.2	0.19 ± 0.002	0.27 ± 0.001	0.32 ± 0.02	7.07 ± 0.23	12.7 ± 0.50	0.73 ± 0.01	15.8 ± 0.66	822 ± 28.6
SSL:W6:4		5.86 ± 0.31	0.42 ± 0.01	0.05 ± 0.002	1.23 ± 0.1	0.09 ± 0.001	0.15 ± 0.001	0.19 ± 0.01	2.17 ± 0.11	4.91 ± 0.43	0.54 ± 0.02	8.25 ± 0.51	138 ± 11.7
BCSSL500	N_2	6.36 ± 0.83	0.30 ± 0.02	0.01 ± 0.001	0.03 ± 0.001	0.05 ± 0.002	0.01 ± 0.001	0.03±0.001	0.32 ± 0.02	0.23 ± 0.01	0.37 ± 0.02	19.8 ± 1.70	765 ± 65.3
BCSSL600		5.14 ± 0.44	0.26 ± 0.01	0.01 ± 0.001	0.04 ± 0.001	0.06 ± 0.003	0.02 ± 0.002	0.01 ± 0.001	0.24 ± 0.01	0.25 ± 0.02	0.98 ± 0.03	5.63 ± 0.64	482 ± 28.9
BCSSL700		4.97 ± 0.61	0.28 ± 0.05	0.01 ± 0.001	0.03 ± 0.005	0.07 ± 0.002	0.01 ± 0.001	0.02 ± 0.001	0.15 ± 0.01	0.21 ±0.01	0.87 ± 0.01	3.75 ± 0.50	106 ± 9.34
BCSSLW8:2 500		3.75 ± 0.21	0.21 ± 0.02	0.01 ± 0.001	0.02 ± 0.002	0.02 ± 0.001	0.02 ± 0.001	0.04 ± 0.001	0.25 ± 0.02	0.14 ± 0.02	0.38 ± 0.01	18.1 ± 2.19	810 ± 73.6
BCSSLW8:2 600		2.47 ± 0.12	0.24 ± 0.01	0.01 ± 0.001	0.03 ± 0.001	0.01 ± 0.003	0.02 ± 0.001	0.02 ± 0.001	0.13 ± 0.01	0.05 ± 0.001	0.71 ± 0.03	5.54 ± 0.77	448 ± 51.9
BCSSLW8:2 700		2.31 ± 0.26	0.05 ± 0.001	0.01 ± 0.001	0.01 ± 0.001	0.01 ± 0.003	0.02 ± 0.001	0.01 ± 0.001	0.03 ± 0.01	0.02 ± 0.002	0.51 ± 0.02	3.69 ± 0.90	115 ± 29.6
BCSSLW6:4 500		3.12 ± 0.31	0.11 ± 0.01	0.02 ± 0.002	0.02 ± 0.002	<DL	<DL	0.02 ± 0.001	0.21 ± 0.02	0.11 ± 0.02	0.30 ± 0.01	12.5 ± 0.92	777 ± 59.3
BCSSLW6:4 600		1.03 ± 0.11	0.24 ± 0.02	0.01 ± 0.001	0.03 ± 0.001	<DL	<DL	0.01 ± 0.001	0.12 ± 0.001	0.02 ± 0.001	0.44 ± 0.03	4.75 ± 0.41	462 ± 32.5
BCSSLW6:4 700		0.30 ± 0.01	0.24 ± 0.01	0.01 ± 0.001	0.01 ± 0.001	<DL	<DL	0.01 ± 0.001	0.01 ± 0.001	0.01 ± 0.002	0.75 ± 0.05	2.12 ± 0.62	102 ± 19.8
BCSSL500	CO_2	4.61 ± 0.21	0.22 ± 0.01	0.01 ± 0.001	0.06 ± 0.002	<DL	<DL	<DL	0.07 ± 0.002	0.18 ± 0.03	0.42 ± 0.02	7.83 ± 0.51	2183 ± 98.7
BCSSL600		3.21 ± 0.20	0.12 ± 0.01	0.01 ± 0.001	0.04 ± 0.004	<DL	<DL	<DL	0.05 ± 0.001	0.21 ± 0.02	0.42 ± 0.03	6.25 ± 0.33	2295 ± 85.1
BCSSL700		0.95 ± 0.02	0.01 ± 0.002	0.02 ± 0.002	0.02 ± 0.001	<DL	<DL	<DL	0.02 ± 0.002	0.03 ± 0.001	0.73 ± 0.06	4.59 ± 1.30	1183 ± 91.3
BCSSLW6:4 500		2.01 ± 0.33	0.10 ± 0.01	0.01 ± 0.001	0.01 ± 0.002	<DL	<DL	<DL	0.08 ± 0.001	0.01 ± 0.001	0.17 ± 0.06	5.6 ± 1.61	4274 ± 259
BCSSLW6:4 600		1.23 ± 0.11	0.02 ± 0.003	0.01 ± 0.001	0.01 ± 0.002	<DL	<DL	<DL	0.02 ± 0.002	0.01 ± 0.002	0.28 ± 0.03	4.77 ± 0.84	2464 ± 127
BCSSLW6:4 700		0.59 ± 0.02	0.03 ± 0.001	0.01 ± 0.003	0.01 ± 0.003	<DL	<DL	<DL	0.01 ± 0.002	0.01 ± 0.001	0.22 ± 0.04	4.91 ± 1.21	1189 ± 98.3

<DL - below the limit of detection

Table 4. Leaching rates (%) of heavy metals in sewage sludge, willow and sewage sludge-derived biochar (BCSSL) and co-pyrolysed sewage sludge with willow (BCSSLW8:4, BCSSLW6:4) at various temperatures (500-700ºC) and different gases (N_2 and CO_2).

Biochars	Gas	Zn	Cu	Cr	Ni	Cd	Pb	Co	Mn	Fe	Ba	B	Al
SSL	-	1.42	0.58	0.36	10.9	28.51	1.69	16.6	8.75	0.37	0.85	27.6	2.73
W		20.0	7.37	12.8	27.3	3.91	15.4	8.93	20.5	8.21	9.60	5.25	5.20
BCSSL500	N_2	0.67	0.23	0.03	0.12	4.46	0.04	0.96	0.27	0.01	0.28	23.3	6.81
BCSSL600		0.50	0.20	0.03	0.14	3.93	0.08	0.99	0.18	0.01	0.69	6.58	3.41
BCSSL700		0.52	0.20	0.03	0.12	4.40	0.05	0.83	0.10	0.01	0.58	4.11	0.73
BCSSLW8:2 500		0.39	0.16	0.03	0.08	1.59	0.09	1.26	0.22	0.01	0.27	20.2	5.24
BCSSLW8:2 600		0.25	0.18	0.03	0.11	0.59	0.07	0.61	0.09	0.01	0.40	6.13	2.18
BCSSLW8:2 700		0.25	0.04	0.03	0.04	0.57	0.07	0.29	0.02	0.01	0.29	3.94	0.56
BCSSLW6:4 500		0.38	0.09	0.07	0.09	-	-	0.77	0.20	0.00	0.24	14.74	2.57
BCSSLW6:4 600		0.18	0.20	0.03	0.15	-	-	0.35	0.09	0.00	0.30	5.03	1.45
BCSSLW6:4 700		0.09	0.19	0.03	0.04	-	-	0.34	0.01	0.00	0.49	2.26	0.29
BCSSL500	CO_2	0.48	0.15	0.03	0.26	-	-	-	0.06	0.01	0.30	8.37	6.93
BCSSL600		0.30	0.08	0.03	0.13	-	-	-	0.03	0.01	0.22	5.11	5.64
BCSSL700		0.09	0.01	0.02	0.06	-	-	-	0.01	0.00	0.40	4.01	2.61
BCSSLW6:4 500		0.22	0.07	0.03	0.04	-	-	-	0.06	0.00	0.13	14.71	8.16
BCSSLW6:4 600		0.14	0.01	0.03	0.04	-	-	-	0.02	0.00	0.19	4.77	4.75
BCSSLW6:4 700		0.07	0.02	0.03	0.04	-	-	-	0.01	0.00	0.14	1.73	1.72