Leaching of potentially toxic elements from biochars intended for soil improvement

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Abstract

The current study investigated the effects of feedstock type and pyrolysis temperature on the leaching of potentially toxic elements (PTEs) (Cu, Zn, Cd, Ni, Cr and Pb) from the biochar. The aim was to find out, which type of biochar would be best suited for soil improvement. Five types of feedstock were used: sewage sludge compost (SSC) (1); the biomass of unfertilized (2) and fertilized with SSC (3) willow (Salix sp. cultivar ‘Tora’); the biomass of unfertilized (4) and fertilized with SSC (5) perennial mugwort (Artemisia dubia Wall.). It was found that the leaching concentrations of PTEs were higher of mugwort-based biochar in comparison to willow-based biochar. However, in the eluates of mugwort-based biochar, the biggest part of PTEs was bound in complexes with dissolved organic carbon. This means that PTEs in the eluates of mugwort biochar were less mobile and less toxic to soil organisms. PTEs leached from the biochar produced at a temperature of 700°C also were mostly in complexes with dissolved organic carbon. The leaching concentrations of PTEs were higher of the biochar produced from plants fertilized with SSC in comparison to the biochar produced from unfertilized plants (p < 0.05).

It is difficult to predict how the process of leaching of PTEs from the biochar would take place if this biochar were to be introduced into the soil. There are many factors that can affect this. It was found that PTEs leaching concentrations of the biochar did not always depend directly on the total concentrations of PTEs in this biochar. However, it is likely that unfertilized plant-based biochar produced at 700°C temperature would be more suitable for soil improvement.

Key words: Artemisia dubia, heavy metals, potentially toxic elements, Salix, sewage sludge compost.

Introduction

The problem of soil depletion and degradation is becoming increasingly urgent all over the world. This problem is also encountered in Lithuania. Actually, unproductive and less favoured areas account for 10.5% (684305.31 ha) of the total land area of Lithuania (The productivity..., 2011; Land Fund of the Republic of Lithuania, http://zis.lt/wp-content/uploads/2017/04/ZF_2017.pdf). There is a need to increase soil fertility in various ways, which can be as follows: no-till farming, crop rotation, liming and cultivation of perennial crops. Perennial energy grasses or short rotation energy plantations can also be grown (Njakou Djomo et al., 2015; Titova, Bakšienė, 2015; Bakšienė, Titova, 2018). In Lithuania, willow (Salix spp.) is grown predominantly in energy plantations (Sakalauskas et al., 2012). The cultivation of various energy crops reduces soil erosion and nutrient leaching (Demo et al., 2014). It also increases humus and organic carbon content as well as improves soil moisture regime (Dimitriou et al., 2012).

Another way of increasing soil fertility, which is increasingly explored, is the incorporation of biochar into the soil (Novotny et al., 2015; Tammeorg et al., 2017; Rasa et al., 2018), which is believed to improve soil structure and moisture regime (Laird et al., 2010; Rasa et al., 2018; Zhao et al., 2018). The incorporation of biochar into the soil decreases nutrient leaching (Laird, Rogovska, 2015; Haider et al., 2016), increases the population of soil microorganisms and their viability (Shareef, Zhao, 2017). Due to the usually high alkalinity of biochar itself (pH 7), its incorporation into the soil decreases soil acidity (Chan et al., 2007; Novotny et al., 2015), which is very useful for it.
One of the signs of soil degradation is low pH. In addition, with increasing pH, heavy metals (potentially toxic elements, PTEs) become less mobile (Liang et al., 2017) and less likely to leach into groundwater. Biochar also enriches the soil with stable carbon and at the same time increases the growth and yield of plants (Kompan et al., 2015; Frenkel et al., 2017). Biochar from energy plants can be used for soil improvement (Rasa et al., 2018).

Another important environmental problem is the utilization of sewage sludge (Kacprzak et al., 2017; Ozdemir et al., 2020). It is possible to produce biochar from sewage sludge or sewage sludge compost and incorporate it into the soil to improve its properties (Lu et al., 2013; Van Wesenbeeck et al., 2014). However, such biochar should be used with caution, as it can contaminate the soil with PTEs (Van Wesenbeeck et al., 2014).

Another method of recycling sewage sludge is composting and using such compost to fertilize energy crops. Sewage sludge compost (SSC) contains useful elements (N, P, Ca, Mg, etc.) for plants (Wierzbowksa et al., 2016; Kacprzak et al., 2017). Later, the biomass of energy crops can be used traditionally, such as burning to get energy. Alternatively, biochar can be produced from the biomass of energy plants (Nasr, 2020), and then such biochar can be incorporated into the soil to improve its properties.

In both cases of the incorporation of biochar in the soil there is a risk of PTEs entering the soil along with biochar. However, not only the total PTEs concentration in the biochar is important, but also what concentrations of PTEs can leach out from it. Biochar with the lowest concentrations of leached PTEs is best suited for soil improvement.

As it has already been mentioned, there is a lot of data in the literature (Lu et al., 2013; Novotny et al., 2015; Rasa et al., 2018) suggesting that the incorporation of biochar into the soil improves its properties. However, it is necessary to control the amounts of substances released into the environment, including soil.

Research is being carried out on PTEs leaching from biochar all over the world (Beesley, Marmiroli, 2011; Mancinelli et al., 2017). The most numerous are the studies related to PTEs leaching from sewage sludge biochar and biochar derived from its compost (Agrafioti et al., 2013; Petkytė, Baltrenaitė, 2015). However, the research carried out on the leaching of PTEs from the biochar produced from willow (Salix sp.) and mugwort (Artemisia dubia Wall.) biomass is new. In addition, these plants are a promising biochar feedstock as they grow quickly and produce large amounts of biomass required to be pyrolyzed (Song et al., 2019). Therefore, it is appropriate to pyrolyze Artemisia spp. biomass into biochar. In addition, mugwort and willow biomass contains high levels of lignin and cellulose (Kryževičienė et al., 2010; Krzyżaniak et al., 2014; Kadžiulienė et al., 2017). This is useful for biochar production and use.

There is currently no legal framework in place for controlling the use of biochar in agriculture in Lithuania. In other European Union (EU) countries, the legal framework governing the use of biochar is diverse. However, in the several documents related to the EU listing recommended physical and chemical limit values for biochar. These include the European Biochar Certificate (EBC, 2012), International Biochar Initiative (IBI, 2014), Biochar Standards, Biochar Quality Mandate and others. All these documents promote responsible use of biochar and monitor the indicators most harmful to soil. Among the proposed parameters for observation are the potentially toxic elements Cr, Cd, Ni, Cu, Pb and Zn. However, even the aforementioned common EU documents offer limit values only for the total concentrations of these elements. They do not yet estimate the amounts of such PTEs that could be leached from biochar if incorporated into the soil. That information is very important from an environmental point of view. There is a lack of data on the potential leaching of PTEs from biochar, and the results of current experiments to be useful in developing threshold values for PTEs leaching from biochar.

The main purpose of the study described in this paper is to assess how the type of feedstock and pyrolysis temperature affect PTEs (Cu, Zn, Cd, Ni, Cr and Pb) leaching from biochar and their forms in the filtrate. This information is very important to find out, which type of biochar is best suited for soil improvement.

Materials and methods

Selection of biochar feedstocks and biochar production. The biochar was produced from five types of feedstock: sewage sludge compost (SSC) (1); the biomass of unfertilized (2) and fertilized with SSC (3) willow (Salix sp. cultivar ‘Tora’); the biomass of unfertilized (4) and fertilized with SSC (5) perennial mugwort (Artemisia dubia Wall.).

Previous studies of Titova (2016) showed that the mentioned plants uptake potentially toxic elements (PTEs) from soil particularly intensively. Dimitriou et al. (2012), Jama-Rodzeńska and Nowak (2012) and Grignet et al. (2020) also found that willow actively accumulates some PTEs from the soil. In this way, the cultivation of willow and mugwort for the production of biochar would reduce the negative impact of sewage sludge compost on the soil. This impact would inevitably occur if the plants were fertilized with SSC. These plants grow very well under temperate climate, including Lithuania (Kryževičienė et al., 2010; Kadžiulienė et al., 2017; Baksienė, Titova, 2018). This means that a lot of feedstock can be obtained easily.

The sewage sludge compost was provided by the company UAB “Biastra Plius” (Lithuania) in the spring of 2018. Plant biomass was provided by Vokė Branch of the Lithuanian Research Centre for Agriculture and Forestry. In this institution, plants were grown on a light textured soil sand loam Haplic Luvisol (WRB, 2014) in the climatic zone of south-eastern Lithuania (54°37ʹ N, 25°06ʹ E).

Willow had been grown for 13 years since 2005. Mugwort had been grown for 6 years since 2012. Willow was fertilized with SSC twice: 1) in the spring of the 8th year of growing with 20 t ha⁻¹ of SSC dry matter (DM), and 2) in the spring of the 12th year of growing with 110 t ha⁻¹ of SSC DM. Mugwort was also fertilized with SSC twice: 1) in the spring of 2012 with 80 t ha⁻¹ of SSC DM, and 2) in the spring of the 5th year of growing with 110 t ha⁻¹ of SSC DM. The willow biomass was harvested in the spring of the 2nd year, 8th year and 12th year of growing. The mugwort biomass was harvested every autumn. For biochar production biomass yield of 2017 was used.

Before the biochar production, the plants were crushed. Then SSC and plants were oven-dried to a constant weight at 105°C. Feedstocks were pyrolyzed in a muffle furnace SNOL 30/1100 E5CK-T (SNOL, Lithuania) under limited oxygen conditions. The heating rate was 10°C min⁻¹ (Lu et al., 2013).

In the described experiment, biochar was produced at 450°C and 700°C temperatures. The residence time in the pyrolysis was 2 hours. Pyrolysis temperatures (low 450°C and high 700°C) were chosen to produce biochars with different properties. There is evidence in the literature (Lu et al., 2013; Gusiatin et al., 2016; Zhao et al., 2018) that pyrolysis temperature greatly affects the physicochemical properties of biochar. A total of ten types of biochar were produced and investigated.
the existing ammonium acetate (NH₄OAc) technique (pH 7), where ammonium (NH₄⁺) is displaced by potassium chloride (KCl), following removal of excess NH₄OAc at pH 7.0, and 3) removal of excess NH₄OAc with 2) extraction of exchangeable cations with 1 M NH₄OAc treatment and sample acidity (pH) adjustment to pH 7.0, and 3) removal of excess NH₄OAc with phosphorus (P) and potassium (K) by a microwave plasma-atomic emission spectrometer 4200 MP-AES (Agilent Technologies, USA). Ammonia was analysed with Nessler reagent colourimetrically on a spectrophotometer UV-VIS Cary 60 (Agilent Technologies, USA) at λ = 460 nm. CEC was calculated as a sum of Ca²⁺, Mg²⁺, Na⁺, K⁺, and NH₄⁺ (Munera-Echeverri et al., 2018).

Hydrophobicity of biochar was investigated using a water drop penetration time test (Doerr, 1998; Usevichiūtė, Baltrėnaitė, 2019). Five grams of crushed homogenized biochar were placed on flat glass plates. Then, using a pipette, 5 drops of deionized water were placed on the surface of the biochar. Using a stop-watch, water drops (all 5 drops) penetration time was recorded. The following categories of hydrophobicity (time) were used: 1) strongly hydrophilic – < 5 s, 2) hydrophilic – 5–10 s, 3) slightly hydrophilic – 10–30 s, 4) slightly hydrophobic – 30–60 s, 5) moderately hydrophobic – 60–180 s, 6) hydrophobic – 180–300 s, 7) strongly hydrophobic – 300–600 s, 8) very strongly hydrophobic – >3600 s.

Potentially toxic elements (PTEs) leaching experiment was performed in the laboratory of Research Institute of Environmental Protection, Vilnius Gediminas Technical University. In order to assess the potential leaching of PTEs (Cd, Pb, Cr, Ni, Zn and Cu) from the biochar to the soil, the up-flow percolation leaching test according to standard BS EN 14405:2017 (Characterization of waste. Leaching behaviour test. Up-flow percolation test (under specific condition) was applied. Ten types of biochar were investigated; two replicates were used. Columns 5 cm in diameter and 30 cm in height were used for the experiment (Pečkytė, Baltrėnaitė, 2015).

The scheme of leaching test equipment (Pečkytė, Baltrėnaitė, 2015; Mancinelli et al., 2016) is shown in Figure 1.

The bottom section of each column was equipped with two filters. The biochar was crushed and then dried to a constant weight. A load of 100 g of such biochar was added to each column. Then the columns were saturated with water by hydrostatic pressure. The water-saturated biochar was left for 3 days to balance the system. Seven eluates were then collected at a constant rate. Each eluate was collected into a separate bottle. The volumes of eluates (L) were determined: 1) 0.01, 2) 0.01, 3) 0.03, 4) 0.05, 5) 0.1, 6) 0.3 and 7) 0.5. They were calculated according to the procedure described in standard BS EN 14405:2017. They depended on the mass (kg) and number of eluates used. The time required to collect each eluate was also recorded during the experiment.

The acidity (pH) of all eluates was then measured using a pH meter Mettler Toledo SevenMulti (Mettler Toledo, USA). Then the eluates were filtered.

PTEs concentrations (mg L⁻¹) and dissolved organic carbon (DOC) (mg L⁻¹) were determined in eluates. Concentrations of PTEs were determined by atomic absorption spectroscopy using a spectrophotometer Buck Scientific 210 VGP (Buck Scientific, USA) equipped with air-acetylene flame (FAAS) or using graphite furnace atomic absorption spectroscopy (GFAS). DOC was determined using a Shimadzu UV/VIS-TOC Analyzer with ASI-V Auto Sampler System (Japan). The results of the analyses were needed to model the forms of PTEs in the eluates. The concentrations of PTEs were subsequently converted to mg kg⁻¹ and % for further analysis.

Concentrations of PTEs in percent were calculated as a percentage of PTEs total concentrations in biochar (Agrafioti et al., 2013).

WHAM modeling. Modeling of PTEs forms in eluates was performed using the Windermere Humic Aqueous Model (WHAM7) for waters (Tipping, et al., 2011; Mancinelli et al., 2017). WHAM7 simulates the chemical processes that occur when metals enter soil and water systems. This model is very important for understanding how pollution can affect the environment and how PTEs bind to humic substances. WHAM7 can be used to predict the activity of free metal ions. It is possible to predict what part of PTEs will be in a free ion form in the eluates and what part of PTEs will be bound in complexes with DOC. Input data in model WHAM7 were: 1) PTEs concentrations (mg L⁻¹) in biochar eluates, 2) pH of biochar eluates and 3) DOC concentrations (mg L⁻¹) in biochar eluates. The temperature during the leaching experiment was 25°C.

Statistical analysis. Each parameter was tested in 2–3 repetitions. Reference materials were also used: the European Reference Material ERM®-CD100 “Trace elements and pentachlorophenol (PCP) in wood” (https://rrr.bam.de/RRR/Content/EN/Downloads/RM-Certificates/RM-cert-environment/erm_cd100e.pdf?__blob=publicationFile) and Sewage Sludge Certified Reference Material LGC6181 (https://www.lgcstandards.com/FR/en/Sewage-sludge-Extractable-metals/p/LGC6181#multianalytetable). The significant differences between the values of parameters of various biochar types were determined using the two-way analysis of variance (ANOVA) for Excel 2000, version 2.2 (Microsoft Corp., USA). Fisher test was used for comparison of data. Significant differences were observed at the 95% probability level. Standard errors were calculated.

Results and discussion

Leaching of potentially toxic elements (PTEs) from biochar. Leaching experiment was carried out with all 10 types of biochar. Having estimated the lead (Pb) leaching from various types of biochar during the experiment (total Pb concentration in all 7 eluate fractions, mg kg⁻¹), it was shown that Pb leaching from SSC biochar was 9 times lower than that from plant-based biochar (p < 0.05) (Fig. 2). Though Pb total concentrations were around 11 times higher in SSC biochar than in the plant-based biochar, it could have been expected that Pb leaching would be equally higher in SSC biochar. It was found that Pb leaching was lower from willow-based biochar in comparison to mugwort-based biochar (p < 0.05). Pb leaching was higher for biochar produced from the biomass of plants fertilized with SSC in comparison to biochar produced from unfertilized plant biomass (p < 0.05). Pb leaching was higher from willow-based biochar produced at 700°C compared to...
that from willow-based biochar produced at 450°C \( (p < 0.05) \). The lowest Pb leaching was observed from SSC biochar (0.037–0.055 mg kg\(^{-1}\); 450°C and 700°C) and from unfertilized willow-based biochar (0.032 mg kg\(^{-1}\); 450°C) (Fig. 2).

SSC biochar contained approximately 15 times higher nickel (Ni) concentrations than plant-based biochar \( (p < 0.05) \). Regardless of this, SSC biochar produced at 450°C had the lowest Ni leaching concentration out of all investigated biochar types, i.e.

\[ \text{LSD}_{0.05} \] least significant difference at the 0.05 probability level; \( n = 2 \); mean value ± SE; SSC – sewage sludge compost

Figure 2. Leaching of potentially toxic elements (PTEs) from biochar

0.85 mg kg\(^{-1}\) \( (p < 0.05) \). Ni leaching concentration of biochar produced from SSC at 700°C was similar or only 1.3 times higher than that of plant-based biochar. This demonstrates that the concentrations of PTEs that can be leached from biochar are not necessarily directly dependent on the total concentrations of the said elements in biochar. Agrafioti et al. (2013) studied Ni leaching from sewage sludge biochar (pyrolysis was performed at 300°C). They also reported very low Ni leaching average concentration – 0.14 mg kg\(^{-1}\) (0.6%). The current study showed that just like in the case with Pb, the leaching percentage of Ni was significantly lower \( (p < 0.05) \) in SSC biochar (1.44–2.22%) in comparison to plant-based biochar (22.4–46.6%) (Fig. 3).

A single trend showing how Ni leaching depends on the species of plant used to produce biochar could not be identified. In many cases, Ni leaching was higher from biochar produced from plants fertilized with SSC in comparison to biochar produced from unfertilized plants \( (p < 0.05) \). Based on these results, it can be concluded that unfertilized plant-based biochar would be more suitable to be incorporated into the soil. It was also found that Ni leaching concentration of SSC biochar produced at 700°C was statistically higher in comparison to SSC biochar produced at a lower (450°C) temperature \( (p < 0.05) \).

Contrary to Pb and Ni, the leaching of chromium (Cr) was 1.5 to 9.3 times higher from SSC biochar (1.85–2.51 mg kg\(^{-1}\)) in comparison to plant-based biochar (0.27–1.27 mg kg\(^{-1}\)) (Fig. 2). However, the total concentration of Cr was as many as 52 times higher in SSC biochar than in plant-based biochar. With the initial Cr concentrations in plant-based biochar being very low (0.78–3.35 mg kg\(^{-1}\)), the resulting leaching percentage of this element from the mentioned biochar was very high. It amounted to as much as 12.5% to 56.8%. Leaching concentrations of SSC biochar was only from 1.7% to 2.7% (Fig. 3). Agrafioti et al. (2013) reported that Cr leaching concentration of sewage sludge biochar (pyrolysis at 300°C) was 0.5% (0.11 mg kg\(^{-1}\)). Peckyé and Baltrénaité (2015) found that Cr leaching concentration of biochar of paper mill sludge (pyrolysis at 450°C and 600°C) was 0.00–0.26% and Cr leaching concentration of leather sludge biochar – 0.23–0.47%. It was also found that Cr leaching was lower from willow-based biochar in comparison to mugwort-based biochar. However, a significant difference \( (p < 0.05) \) was observed only in the case of the biochar produced at 700°C (Fig. 2).

The experiment also evaluated the effect of the fertilization of plants with SSC on the leaching of Cr (mg kg\(^{-1}\)) from the biochar made of these plants. It was found that fertilization increased Cr leaching when the pyrolysis temperature was 450°C and decreased leaching when it was 700°C \( (p < 0.05) \). No single trend showing the impact of pyrolysis temperature on the Cr leaching from the biochar was found. The results showed that the lowest leaching of Cr was observed from biochar produced at a pyrolysis temperature of 450°C from unfertilized willow and unfertilized mugwort \( (p < 0.05) \).

The study found that the average total concentration of copper (Cu) in SSC biochar was approximately 15 times higher than that in plant-based biochar. Regardless of this, Cu leaching from SSC biochar (0.084 mg kg\(^{-1}\)) was twice lower \( (p < 0.05) \) than in the case of plant-based biochar (0.175 mg kg\(^{-1}\)) (Fig. 2). As a percentage, Cu leaching from SSC biochar (0.053% on average) was also significantly lower \( (p < 0.05) \) than from plant-based biochar (1.65% on average) (Fig. 3).

Beesley et al. (2010) noticed that leaching of Cu, first of all, was influenced by the concentration of DOC in the biochar. However, the previous studies of the authors (Titova, Baltrénaitė-Gedienė, 2020; in press) showed that average DOC concentration in SSC biochar was two times lower than in plant biochar.
biochar was more intensive \( (p < 0.05) \). However, Cd leaching from mugwort-based \( (Gusiatin et al., 2016; Liang et al., 2017) \).

\[ \text{pH} \text{ of SSC biochar can possibly reduce the mobility of surface area, pore structure or DOC values of the biochar are lower or similar to those from plant-based biochar. It the leaching concentrations of PTEs from SSC biochar \( \times \text{lower from SSC biochar than from plant-based biochar. However, Cd leaching concentration was } 16 \text{ times lower from SSC biochar than from plant-based biochar.} \]

\[ \text{Cd concentration of SSC biochar was found as was the case with many other previously investigated elements. Cd concentration from the biochar produced at } 700^\circ C \text{ was only } 0.011 \text{ mg kg}^{-1}. \]

\[ \text{Zn leaching from SSC biochar was on average only 1.2 times higher than from plant-based biochar. Such a low level of leaching of Zn from SSC biochar could be explained by its high pH.} \]

\[ \text{Beesley et al. (2010) confirmed this tendency. Peckýte and Báltrenaitė (2015) also reported that Zn leaching concentration from the biochar of paper mill sludge and from leather sludge biochar (pyrolysis at } 450^\circ C \text{ and } 600^\circ C \text{ was } 0.12\text{–}0.44\%. Of SSC-fertilized willow-based biochar, Zn leaching concentration was higher than that from plant-based biochar (Fig. 3).}\]

\[ \text{The increase in pyrolysis temperature reduced Zn leaching from SSC biochar and from biochar produced from SSC-fertilized willow and mugwort (} p < 0.05 \). The lowest Zn leaching concentrations were observed of unfertilized willow-based and SSC-fertilized mugwort-based biochars (} p < 0.05 \).

\[ \text{Beesley and Marmiroli (2011) reported that biochar can } 500\text{-fold reduce Cd concentration and } 45\text{-fold reduce Zn concentration in the leachate of contaminated soil. However, Cd and Zn can also be leached out from the biochar itself. In the current study, cadmium (Cd) leaching from SSC biochar was compared with that from plant-based biochar. A similar tendency was found as was the case with many other previously investigated elements. Cd concentration of SSC biochar was on average 9 times higher than from plant-based biochar. However, Cd leaching concentration was 16 times lower from SSC biochar than from plant-based biochar (} p < 0.05 \).} \]

\[ \text{Further research is required to determine why the leaching concentrations of PTEs from SSC biochar are lower or similar to those from plant-based biochar. It may be related to the pH, Brunauer-Emmett-Teller (BET) surface area, pore structure or DOC values of the biochar itself (Agrafioti et al., 2013; Liang et al., 2017).} \]

\[ \text{High pH of SSC biochar can possibly reduce the mobility of PTEs thus inhibiting their leaching to the environment (Gustat et al., 2016; Liang et al., 2017).} \]

\[ \text{According to this study, the pH of mugwort-based biochar was higher than that of SSC biochar (} p < 0.05 \). However, Cd leaching from mugwort-based biochar was more intensive (} p < 0.05 \). Beesley et al. (2010) also noticed that it is difficult to elucidate all processes, which influence Cd and Zn mobility. In any case, it is important to note that high concentrations of PTEs in biochar do not necessarily result in high leaching concentrations of PTEs from that type of biochar. Conversely, low concentrations of PTEs in biochar do not prevent significant leaching of these elements from biochar. For example, in the case of plant-based biochar, the leaching percentage of Cd contained by it was 3.8\% to 41.3\%, in the case of SSC biochar, the percentage was only 0.05\% to 0.2\% Cd (Fig. 3). Also, it was found that Cd leaching was statistically lower for biochar produced from SSC-fertilized willow in comparison to biochar produced from SSC-fertilized mugwort (} p < 0.05 \).} \]

\[ \text{Cd was the only investigated PTE that showed a decrease in leaching concentration of different types of biochar when temperature increased (} p < 0.05 \). This happened because Cd is released from biochar to the environment during pyrolysis at } 700^\circ C \text{ (Van Wesenbeeck et al., 2014; Gusieniény et al., 2016). The leaching experiment showed that the increase in pyrolysis temperature usually decreased Cd leaching from biochar.} \]

\[ \text{In summary, it was found that the leaching concentrations of Pb, Cr and Cu were lower of willow-based biochar than those of mugwort-based biochar. The leaching concentrations of Ni and Cd were lower of the biochar produced from SSC-fertilized willow in comparison to the biochar produced from SSC-fertilized mugwort. It was found also that in many cases the leaching of investigated PTEs was higher from the biochar produced from plants fertilized with SSC in comparison to the biochar based on unfertilized plants (} p < 0.05 \). This means that biochar produced from unfertilized plants is more suitable for soil improvement.} \]

\[ \text{The leaching percentage of Pb, Ni, Cr and Cd from plant-based biochar was high (3.8–50.1\%); however, it was low for Cu and Zn – only 0.076–2.89\% (Fig. 3). For all tested PTEs, leaching from SSC biochar as a percentage was much lower (only 0.012–2.75\%) than that from plant-based biochar. Also, although Agrafioti et al. (2013) reported that leaching of Cr, Ni, Cd, Cu and Pb from sewage sludge biochar (pyrolysis at } 300^\circ C \text{) was only 0.1–4.0\% (lower than 0.74 mg kg}^{-1}. \text{). Though, during the previous studies by the authors (Titova, Baltremenaitė-Cedienė, 2020; in press) PTEs concentrations in SSC-derived biochar were found to be above limit concentrations prescribed according to EBC (2012). As a result, SSC-derived biochar is not suitable for incorporation into the soil with the aim of improving its properties. It was not possible to identify any plant-derived biochar with the lowest leaching concentrations (\%) for all investigated PTEs (Fig. 3). The leaching of PTEs as a percentage was lower from the biochar produced at } 700^\circ C \text{ in comparison to produced at } 450^\circ C. \text{ Only Cd showed the opposite trend (} p < 0.05 \).} \]

\[ \text{Modeling of forms of PTEs in eluates. Modeling with WHAM/Model VII (version for waters) showed that the increase in pyrolysis temperature can decrease the levels of PTEs in a free ion form in biochar eluates. This means that it can increase the levels of} \]
PTEs bound in complexes with DOC in biochar eluates. As a result, PTEs become less mobile and less toxic to microorganisms, plants, etc.

In the eluates of SSC biochar (450°C and 700°C) and unfertilized willow- and mugwort-based biochar produced at 450°C, PTEs were mostly in the form of free ions (>0.8) (Fig. 4). This may be related to the fact that these eluates had the lowest pH from 7.8 to 9.2. The pH of the eluates of other types of biochar was from 9.8 to 11.3. In the eluates of biochar produced from SSC-fertilized mugwort and willow (450°C) and from unfertilized and SSC-fertilized mugwort (700°C), the levels of PTEs in the form of free ions were the lowest.

Modeling results showed that the elements that can be most often found in a free ion form (>0.9) in the eluates of various types of biochar are Cd and Ni (Fig. 4). It is likely that the free ion form of Cr is very rare in the eluates of all types of biochar. In other words, it is assumed that the majority of Cr leached from biochar will be bound to DOC (Tipping et al., 2011). Based on the analysis of results obtained by modeling the forms of elements in the eluate, it is recommended using mugwort-based biochar (700°C) as a soil amendment, because it has the lowest part of PTEs in a free ion form in its eluates.

**Physical and chemical properties of biochar.**

In order to better understand, which type of biochar is most suitable for soil improvement, the cation exchange capacity (CEC) and hydrophobicity of biochar were investigated. The biochar produced at 700°C was found to have a statistically significantly higher CEC (42.6–66.9 cmol kg\(^{-1}\)) compared to that produced at 450°C (32.4–63.6 cmol kg\(^{-1}\)) \(p < 0.05\) (Fig. 5). Gusiatin et al. (2016) studied the biochar produced from maize silage, sewage sludge compost, wooden pellets and digestate (2016) and found that the biochar produced from maize silage had a statistically higher CEC (42.6–66.9 cmol kg\(^{-1}\)) compared to that produced at 450°C. They also investigated the effect of pyrolysis temperature on the hydrophobicity of different types of biochar. It was found that not always at higher pyrolysis temperatures the CEC of biochar was higher. It was also found that the mugwort-based biochar exhibited a higher CEC (53.4–66.9 cmol kg\(^{-1}\)) compared to the willow-based biochar (34.8–43.2 cmol kg\(^{-1}\)) \(p < 0.05\).

The analysis of CEC and hydrophobicity confirmed the results of previous studies by the authors (Titova, Balténaïtė-Gedienė, 2020; in press): the biochar produced at 700°C is more suitable for soil improvement. The biochar with higher CEC is more useful for soil quality improvement. The higher the CEC, the more pollutants (including PTEs) can be adsorbed by biochar from the soil. Based on this, the authors concluded that the biochar produced from sewage sludge compost (SSC) is more suitable for soil improvement.

**Conclusions**

1. The concentrations of Pb, Ni, Cr, Cu, Zn and Cd leached from the biochar were not directly proportional to the initial total concentrations of these elements contained in the biochar.
2. The leaching of potentially toxic elements (PTEs) was higher from the biochar produced from plants fertilized with sewage sludge compost (SSC) in comparison to the biochar produced from unfertilized plants \(p < 0.05\).
3. In most cases, the leaching concentrations of PTEs were lower of willow-based biochar in comparison to mugwort-based biochar. However, in the eluates of mugwort-based biochar, the part of PTEs in the form of free ions was the lowest.
4. No single trend showing the impact of pyrolysis temperature on the leaching of investigated PTEs from biochar was found. However, modeling results showed that the increase in pyrolysis temperature can decrease the part of PTEs in a free ion form in biochar eluates.

5. The highest cation exchange capacity (CEC) was observed in mugwort-based biochar (pyrolysis was performed at 700°C). More hydrophilic was biochar produced at 700°C.

6. Based on the analysis of all data, biochar from unfertilized plants (pyrolysis at 700°C) would be most suitable for use in soil improvement.

Acknowledgements
This project has received funding from European Social Fund (project No. 09.3.3-LMT-K-712-02-0030) under grant agreement with the Research Council of Lithuania (LMTLT).

References
Potencialiai toksiskų elementų išplovimas į dirvožemį pagerinti skirtos bioangles

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Santrauka
Tirta žaliavos tipo ir pirolizės temperatūros įtaka potencialiai toksiskų elementų (PTE) Cu, Zn, Cd, Ni, Cr ir Pb, išplovimui į bioangles. Tyrimo tikslas – nustatyti, kokios bioangles tipo būtų tinkamiausias dirvožemio gerinti. Naudotos penkių rūšių žaliavos: nuotekų dumblo kompostas (1), veislės ‘Tora’ netręstų (2) ir tręstų nuotekų dumblo (3) gluosnių (Salix sp.) biomasė, netręstų (4) ir tręstų nuotekų dumblo (5) pavėsinių (šiaudų, žalių, įsimėdėjusių augalų ir kt.) nuėmimo ir įtakos gali turėti daugelis veiksnių. Nustatyta, kad bioangles PTE išplovimo koncentracijos ne visada tiesiogiai priklauso nuo suminių šioje bioanglyje esančių PTE koncentracijų; tačiau dirvožemio organizmams gali būti tinkamiau skirtos bioangles, įdirvožemį pagerinti galbūt labiau tiktų šios kiečių (Artemisia dubia Wall.) biomasė.

ISSN 1392-3196 / e-ISSN 2335-8947

Leaching of potentially toxic elements from biochars intended for soil improvement

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ISSN 1392-3196 / e-ISSN 2335-8947