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Research paper

Trace element leaching from contaminated willow and poplar biomass – A laboratory study of potential risks

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A B S T R A C T

Despite the advantages of phytoextraction, serious risks can be caused by the produced contaminated biomass. Currently, there is a lack of research on the potential risk of storing and handling this biomass. The aim of our study was to verify the losses of potential risk elements (Cd, Cu, Fe, Mn, Pb, Zn) via leaching of short rotation coppice biomass in laboratory batch tests. Harvested woody and leafy biomass was chipped and/or kept compact. The fresh and/or dried biomass was then leached by two types of leachate to simulate rainfalls—neutral water and/or acidified water. Chipped wood was characterised by the highest element release in comparison to whole branches. The leaves were considered more risky from the point of view of element losses. A similar trend of leaching was observed for all elements, except iron. More iron was leached from fresh wood biomass, whilst in the case of the leaves, iron was leached more from dry biomass. Lead was released by 1.4–7.2% from the biomass. Cadmium was leached by 2% from woody biomass, but up to 39% from leaves. The potential losses of these elements during storage and pre-processing should be taken into account in the development of methodologies for the storage and handling of contaminated biomass before its' processing.

1. Introduction

In situ remediation technologies such as phytoextraction, where plants remove contaminats from the environment or make pollutants less harmful, are measures for environmentally friendly restoration of contaminated soil [1]. For induced plant growth on a contaminated site, the choice of plant species is primarily based on plant properties such as their ability to accumulate risk elements into their tissues and the ability for high biomass production. Thus, fast-growing trees are suitable and can be further used for energy purposes. This sustainable process of plant cultivation for soil remediation connected with further biomass utilisation is only possible when the contaminant recovery into the environment is eliminated [2]. The potential of willow for risk element phytoextraction technologies was observed, for instance, on heavily and moderately polluted calcareous soils [3], moderately contaminated Cambisol [4], and sandy atmospherically contaminated soil [5]. Ruttens et al. [6] investigated the possibilities of growing willows and poplars under short rotation coppice (SRC) on acid, poor and sandy metal-contaminated soil to combine phytoextraction and production of biomass for energy purposes.

Despite all the advantages of phytoextraction, there is a potential for element losses between harvest and processing of the contaminated biomass (including pre-treatment and storage) to the environment. In the scientific literature, there is a lack of essential information on how to handle and store this kind of biomass suitably before its use for energy purposes, to avoid the risk of element release back into environment. A two-phase harvest of biomass is usually provided on small plantations. Biomass is firstly cut and then left to dry to moisture of 20–30% at the edge of the plantation. After drying, the biomass is chipped. Biomass is sufficiently dried (30% moist) and has a higher energy value [7,8]. For one-phase harvest, special technology is used, e.g. a modified corn cutter providing a stern cut and immediate chipping. The drawback of this procedure is a possible problem with the storage of moist chips (up to 50%), but this material is more suitable for manipulation and transportation [7,8]. Moreover, Kofman and Spinelli [9] confirm that the storage of willow biomass from short rotation coppice is very difficult. They observed loosing of large amount of storing fine chips dry matter and their heavy colonisation of microorganisms.

Leaching tests are common tools for assessing constituent release upon contact with water and usually two types are performed: static and dynamic extraction tests. In static extraction protocols (batch tests), leaching takes place with a single volume of leachant. In dynamic extraction protocols, the leaching fluid is renewed throughout the test

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[10]. In our study, we chose the batch extraction according to ČSN EN 12457–1 (838005): Waste characterisation - Leaching - Verification of leachability of granular waste and sludge, because of absence of other suitable test according to the Czech legislative.

The leaching of various elements from element-loaded biomass is discussed in the context of potential phytomining of the elements [11]. The methods available for the recovery of the contaminated biomass processing were reviewed by Kikucha and Tanaka [12]. For biomass that has no 'ore value', the disposal in landfills or hazardous waste landfills is recommended with volume reduction by processes such as composting and anaerobic digestion [13].

There is insufficient knowledge on the storing of biomass from phytoremediation technology. Thus, two main questions considering the handling and storage of contaminated biomass were posed: i) is it more suitable to make chips of larger branches after harvesting? ii) is it more suitable to store fresh or dried biomass from the point of view of element release? The aim of our study was to provide a laboratory test to verify the potential loss of elements (Cd, Cu, Fe, Mn, Pb, Zn) via leaching during the storage of short rotation coppice biomass. The main target was to simulate the conditions of biomass storage and observe their influence on elemental leaching. Harvested woody and leaf biomass was chipped and/or kept compact. Different conditions of simulated storing were set, these were: i) biomass was kept fresh and/or dried, and ii) two types of leachate were chosen to simulate rainfalls—neutral water and/or acidified water.

2. Materials and methods

2.1. Plant biomass

Plant biomass originating from a phytoextraction plantation was chosen for the experiment. One clone of willow and one clone of poplar, were tested, these were: *Salix x smithiana* (S) and *Populus nigra* x *Populus maximowiczii* (P). The field phytoextraction experiment was established on multi-heavy metal (predominantly Cd, Pb, and Zn) contaminated soil near the village of Podlesí (49°42′24″N, 13°58′32″E) close to the town of Příbram, 58 km south of Prague, Czech Republic. This area has been described as one of the most polluted sites in the Czech Republic [14]. The soil type is a modal Cambisol, weakly acidic (pH_{H2O} is 5.66 and pH_{KCl} is 5.27) with a CEC of 166 mmol kg^{-1}. Pseudototal content (extracted by *aqua regia*) of cadmium in an arable layer is 83 mg kg^{-1}, lead 1214 mg kg^{-1} and zinc 218 mg kg^{-1}.

2.2. Leaching experiment and analytical methods

The leaves and branches of willows (S) and poplars (P; both fast growing trees) were leached as a fresh biomass immediately after harvest and as a dry biomass. Note that after drying at 65 °C, the tested biomass was not affected by any biological transformation during storage. Both fresh and dry biomass of branches was leached as: i) 20 cm long branches, and ii) as 2 cm chips. The branches were sealed with wax at their cut ends to simulate storage of whole branches and to observe the risk elements release just through the bark. The chips were not treated, therefore, and the storage of fresh and dry wood chips was simulated. The branches were leached in 1 L PE laboratory bottles (round, wide-mouth bottles, Kartell, Germany), the chips in 250 mL PE laboratory bottles (round, wide-mouth bottles, Kartell, Germany). Fresh and dried leaves were leached both whole and cut into small pieces. The extraction agents were: i) deionised water (pH = 7) and, ii) 0.5 mmol L^{-1} H_2SO_4 (pH = 3) simulating extremely acid rainfall. Water was boiled before the experiment, to avoid CO_2 in the agent and to keep deionised water at pH 7. The ratio was 1:2: 1 kg of dry matter equivalent was treated with 2 L of leaching. The mixtures were agitated on a reciprocating shaker for 24 h (160 rpm) and filtered (filtered paper for qualitative analyse, Macherey-Nagel, MN 615 70 g m^{-2}). The temperature was kept at 25 °C during the whole process. The leaching test performed in our study did not include the control of pH. Each tested treatment was conducted in 3 replicates.

For the determination of the total element content in the wood of plants, the dry biomass samples were ground using a stainless steel mill. A dry ashing procedure [15] was applied for sample decomposition. An Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-OES, Agilent 720, Agilent Technologies Inc. USA) equipped with a two-channel peristaltic pump, a Struman-Masters spray chamber, and a V-groove pneumatic nebuliser made of inert material was applied for the determination of Cd, Cu, Fe, Mn, Pb, and Zn in the plant leachates and digest. The experiment used a power of 1.2 kW, plasma flow of 15.0 L/min, auxiliary flow of 0.75 L/min and nebuliser flow of 0.9 L/min. Certified reference material, NCS DC 73348 Bush Branches and Leaves, was applied for quality assurance of the analytical data. This material was certified to contain the following: Zn: 20.6 ± 2.2 mg kg^{-1}; Cd: 0.14 ± 0.06 mg kg^{-1} and Pb:7.1 ± 1.1 kg^{-1} was determined: Zn: 19.4 ± 2.1 mg kg^{-1}; Cd: 0.15 ± 0.08 mg kg^{-1} and Pb:6.9 ± 1.4 mg kg^{-1}.

2.3. Data analysis

All of the statistical analyses were performed using the Statistica 10.0 (www.statsoft.com) and CANOCO 4.5 programmes. All data were checked for homogeneity of variance and normality (Levene and Shapiro-Wilk tests). Collected data were evaluated by ANOVA. Principal Component Analysis (PCA) was applied to all collected data (concentrations of elements in the wood and bark as well as biomass yield) using the CANOCO 4.5 programme. We used standardised 'species data' because data of a different character and units were analysed together. The PCA was used to make visible correlations between all analysed data and similarities of different clones. The results were visualised in the form of a bi-plot ordination diagram using the CanoDraw programme.

3. Results

3.1. Elements concentration in plants

Total element contents in dry above-ground biomass of willows and poplars in the individual parts of plants are given in Table 1. Higher concentrations of observed elements were determined in the leaves in comparison to branches in all cases, except the content of lead in

Table 1
Total element contents in tested leaves and branches of willows (S) and poplars (P).

Plant part	Type of tree	Cd	Cu	Fe	Mn	Pb	Zn
		mg.kg^{-1}					
Leaves	S	56.9 ± 0.7	5.7 ± 0.1	87.8 ± 2.3	343 ± 10.7	51.0 ± 1.4	725 ± 7.6
	P	28.1 ± 0.2	4.4 ± 0.1	114 ± 8.1	92.7 ± 3.1	46.2 ± 1.0	577 ± 7.0
Branches	S	21.5 ± 10.1	4.3 ± 0.9	15.5 ± 3.1	13.3 ± 1.2	25.2 ± 6.6	197 ± 5.1
	P	15.3 ± 0.65	3.0 ± 0.1	24.1 ± 2.2	11.1 ± 5.1	60.4 ± 9.0	132 ± 4.2

Data are means ± standard error; calculated from three replicates.