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Sustainable Land Management: Growing Miscanthus in Soils Contaminated with Heavy Metals

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Abstract

Miscanthus grows well in some marginal and contaminated soils, and it has the potential to be used as a biofuel. Copper and cobalt are heavy metals that sometimes are present as contaminants in soils at concentrations that may impact the safety of products that are harvested. Laboratory research has been conducted with *Miscanthus sacchariflorus M.* to investigate metal uptake of copper and cobalt because metal concentrations in the harvested parts of miscanthus are important for biofuel applications. The results show that the use of miscanthus for biofuel from soil contaminated by heavy metals depends mainly on the nature of contaminated metals: cobalt was detected only for highest treated concentration of metal and mainly in the roots. The highest concentration of copper was detected in the roots however this metal was detected in stems and leaves of miscanthus as well. Miscanthus biomass harvested from cobalt contaminated soil may be used for energy production because the harvested part accumulated only limited traces of the metal. The experimental results are in reasonable agreement with other results from the literature.

Keywords

Phytoremediation, Miscanthus, Biomass, Heavy Metals, Cobalt, Copper

1. Introduction

There is currently significant interest in sustainable land management, bioenergy crops such as miscanthus, and

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methods to improve quality and productivity in contaminated soils [1]-[31]. This manuscript considers the benefits associated with growing miscanthus on land that has metal contamination with the goals of both harvesting a crop of commercial value as a biofuel and improving soil quality by adding organic carbon and reducing the availability of the metal contaminants. Recently, the literature related to miscanthus production in contaminated soils has been reviewed [22]. Miscanthus can grow and be productive in many contaminated soils, and metal uptake by miscanthus is low, which allows the harvested biomass to be used as a biofuel.

Sustainable land management is about all interests on land, including secure tenure, the reduction of land contamination, and the improvement of land quality including remediation. Sustainable contaminated land management is based on two main issues: selection of the most appropriate technology [31] and using principles of sustainability [18]. Phytoremediation is relatively cheap, ecologically friendly, and effective for large areas with small and medium concentration of contaminants [3] [11] [14] [28].

There are 250,000 contaminated sites within European Union which require urgent attention [5]. In the US the number of Superfund sites is estimated as 1289 in 2011 [27] and a significant amount of metal contaminated land is reported in Southeast Kansas and in Missouri that needs to be remediated and used productively. In Ukraine, intensively and medium-contaminated places are widely spread across the country, the biggest numbers are located at industrially developed East [15]. In Slovakia large brownfields are at the former military places, the former mining production sites and relatively less contaminated sites are located at agricultural regions which have smaller sizes [24].

A growing number of publications are currently focused on the union of two processes: phytoremediation and production of biofuel crops [6] [7] [10] [13] [16] [20]-[22] [25] [26] [30]. The main reason of this phenomena is about increasing demand for biomass production as alternative energy sources and possibility to restore marginal land and brownfields to agricultural food crop use.

Second generation biofuel crops include short rotation trees and annual/perennial grasses; among perennial grasses miscanthus is considered to be the most promising biofuel plant. This crop is native from Southern Asia [2], has a good adaptive potential in European Union countries and USA, and has high harvest yields, in addition miscanthus may be grown in relatively poor soils [26].

Miscanthus was already introduced in Europe and the US and exhibited good production properties [10] [19], plant yields have been documented to be intermediate between native, warm-season grasses switchgrass (*Panicum virgatum L.*), big bluestem (*Andropogon gerardii Vitman*) and annual crops (sorghums, maize) over several years in Kansas [23]. Miscanthus was used for phytoremediation of land contaminated after Chernobyl catastrophe in Ukraine [13] and mining brownfields in Slovakia [7]. The further practical use of miscanthus for energy production and phytoremediation of contaminated sites looks promising in terms of cost and real chances to be accepted in comparison with using expensive conventional remediation. Research has shown that utilization of the biomass obtained as an energy resource is attractive [4] and can turn phytoremediation into a profit making operation [14].

Because metal uptake in miscanthus is often less than with some other plants, there is a need to focus on the reduction of bioavailability of the metals and the very slow removal associated with this perennial crop. The reduction of wind blown dust and soil erosion due to water are benefits associated with establishing miscanthus on metal contaminated land.

Copper and cobalt are considered in this manuscript because new experimental data have been obtained, and these substances are commonly found in contaminated soils. Ames and Prych [1] reported values for cobalt from 8 to 48 mg/kg with an average value of 20 mg/kg for 37 measured values that were from different locations in the state of Washington. For copper, the values ranged from 13 to 120 mg/kg with an average value of 36 mg/kg. These are considered to be values from soils that are not considered to be contaminated.

For developing this technology using miscanthus, the following important parameters have to be subjects of research: impact of nature and concentration of contaminated substances, kinetics of the phytoremediation process, influence of agricultural conditions on perennial crop growth and effectiveness.

This article presents data about impact of contaminated substances and their concentration in miscanthus. The fate and transport of the contaminants during one year of miscanthus growth was investigated.

2. Materials and Methods

The investigation using miscanthus was done during year 2012 and *Miscanthus sacchariflorus M.* was used for the research. The bush of the plant was planted in the open soil in Banska Bystrica, Slovakia in October, 2011 and periodically watered when necessary. After the winter 2011-2012, on May 11th, 2012 the bush was divided into separated plants and each was consequently planted in a separate pot filled with 350 g of soil. The soil used had the following characteristics:

Total nitrogen (in a form of N) content (% max): 1.9;

Total phosphorus content (in a form of P_2O_5) (%max): 0.5;

Total potassium content (in a form of K_2O) (%max): 0.7;

pH: 4.5 - 6.0;

Electrical conductivity (mS/cm): 0.8.

Plants were allowed to be adapted in the soil during two months and were watered if necessary by tap water. Picture of the growing plants from May 11th, 2012 is presented as **Figure 1**. On June 26th, 2012 visually similar plants were selected for the laboratory research.

On July 14th soil in each pot was treated with 50 ml of solution of chemical substances. For the treatment of the soil two soluble metal solutions were selected: cobalt-content soil $CoCl_2 \times 2H_2O$ and copper-content soil $CuSO_4 \times 5H_2O$. Those particular substances were selected as model ones taking into account that both metals are present as contaminants in the soil in Slovakia [24] and Ukraine [21], however, they have different properties [11].

Solutions were prepared using distilled water with different content of substances: 200 mg/l; 400 mg/l and 800 mg/l for $CoCl_2 \times 2H_2O$ and 400 mg/l and 800 mg/l for $CuSO_4 \times 5H_2O$. 50 ml of solutions were added carefully to each pot with planted miscanthus. Simultaneously for each research concentration and duration of treatment two parallel pots with miscanthus were investigated. Plants treated by solutions of selected substances are pictured as **Figure 2** from July 19th, 2012, 5 days after treatment.

Plants were watered by tap water as needed.

On August 16th, 2012, 32 days after the treatment, the first sampling was done. Plants were taken from pots, cleaned from the soil, and dryed in the open air (at the temperature 25˚C - 30˚C) during one week. Then for each plant roots, leaves and stems analysis of metal content was done.

On October 8th, 2012, 86 days after the treatment, the second test was taken (miscanthus plants as for that time are presented as **Figure 3**). The treatment of the plants was the same as described above.

Detection of copper or cobalt in the plant parts were done by using Spectrometer AAS AVANTA Σ by GBC Scientific with the electrothermal atomization. Autosampler PAL 3000 was used for electrothermal analysis. Analysis of the results was supported by software GBC Avanta ver.2.0.

Figure 1. Miscanthus plants after being transplanted into pots on May 11, 2012.

Figure 2. Miscanthus plants on July 19, five days after treatment with contaminated solution.

Figure 3. Miscanthus plants on October 8, 2012, 86 days after treatment with contaminated solution.

3. Results and Discussion

The data about content of metal in miscanthus are presented in **Table 1** and **Table 2** for cobalt-treated plants and in **Table 3** and **Table 4** for copper-treated plants. Analysis of the data shows that selected metals have different uptake behavior.

In case of cobalt-contaminated soil after 32 days of miscanthus growth, cobalt is detected only in miscanthus roots and only for the highest treated concentration. For less treated concentrations after 32 days of treatment metal was not detected in any of parts of miscanthus plants. The coefficient of process effectiveness K was calculated using approach similar to that proposed by [12]. The value of coefficient K was calculated as following:

$$\text{Coefficient K} = \frac{\text{Concentration of metal in plant} \times 100\%}{\text{Concentration of metal in soil}}$$

Table 1. Concentration of Co in miscanthus plants 32 days after soil treatment by solution of $CoCl_2 \times 5\ H_2O$.

Concentration of Co in soil, ppm	Parallel tests, concentration in roots, ppm		Average	Coefficient K	Parallel tests, concentration in stems, ppm		Average	Coefficient K	Parallel tests, concentration in leaves, ppm		Average	Coefficient K
	1	2			1	2			1	2		
10.16	ND*	ND	ND	-	ND	ND	ND	-	ND	ND	ND	-
20.32	ND	ND	ND	-	ND	ND	ND	-	ND	ND	ND	-
40.64	0.43	0.62	0.525	1.29	ND	ND	ND	-	0.03	ND	0.03	0.07

*Not detected.

Table 2. Concentration of Co in miscanthus plants 86 days after soil treatment by solution of $CoCl_2 \times 5H_2O$.

Concentration of Co in soil, ppm	Parallel tests , concentration in roots, ppm		Average	Coefficient K	Parallel tests, concentration in stems, ppm		Average	Coefficient K	Parallel tests, concentration in leaves, ppm		Average	Coefficient K
	1	2			1	2			1	2		
10.16	ND	ND	ND	-	ND	ND	ND	-	ND	ND	ND	-
20.32	0.44	0.62	0.53	2.61	ND	ND	ND	-	ND	ND	ND	-
40.64	0.84	0.81	0.825	2.03	0.05	ND	0.05	0.12	0.02	ND	0.02	0.05

Table 3. Concentration of Cu in miscanthus plants 32 days after soil treatment by solution of $CuSO_4 \times 5H_2O$.

Calculated concentration of Cu in soil, ppm	Parallel tests , concentration in roots, ppm		Average	Coefficient K	Parallel tests, concentration in stems, ppm		Average	Coefficient K	Parallel tests, concentration in leaves, ppm		Average	Coefficient K
	1	2			1	2			1	2		
14.63	2.40	3.60	3.00	20.51	1.20	2.20	1.70	11.62	2.10	2.00	2.05	14.01
29.26	7.20	4.60	5.90	20.16	1.00	2.00	1.50	5.13	3.20	7.20	5.20	17.77

Table 4. Concentration of Cu in miscanthus plants 86 days after soil treatment by solution of $CuSO_4 \times 5H_2O$.

Calculated concentration of Cu in soil, ppm	Parallel tests , concentration in roots, ppm		Average	Coefficient K	Parallel tests, concentration in stems, ppm		Average	Coefficient K	Parallel tests, concentration in leaves, ppm		Average	Coefficient K
	1	2			1	2			1	2		
14.63	7.40	No data	7.40	50.58	1.00	2.40	1.70	11.62	2.60	2.00	2.30	15.72
29.26	6.30	10.20	8.25	28.19	5.00	7.20	6.10	20.85	6.80	7.40	7.10	24.26

The calculated coefficient K is presented in **Tables 1-4**. It may be concluded that for cobalt rather small coefficient K equals 1.29% for roots was received and 0.07% for leaves after 32 days of experiment.

In case of longer growing of plants in contaminated soil (equal to 86 days) metal appeared in miscanthus plant at the middle concentration of initial treatment, but this effect occurred only for roots. In case of highest treated concentration cobalt is detected in all parts of miscanthus: roots, leaves and stems, but in very low concentrations. Respectably, the calculated coefficient K is: 2.03% for roots, 0.12% for stems and 0.05% for leaves. It may be summarized, that in case miscanthus growing in cobalt-contaminated soil with the metal concentration up to 25.1 mg/kg soil the harvested plant may be used for biofuel production without any doubt because it does not contain contaminated metal. If the concentration of cobalt in the soil is higher than 20.32 mg/kg soil, concentration of metal in harvested plant is still very low and plant may be used as biofuel as well.

The fully different behavior was observed for miscanthus when it was grown in soil containing copper. In that case metal is detected in all parts of miscanthus in both determined periods of observation: 32 days and 86 days. The highest concentrations and values of coefficient K were found for roots; the concentrations of copper in leaves and stems are also rather high.

In case of copper a higher coefficient of extraction was found for longer time of treatment-86 days, however this fact is not so evident as for treatment of cobalt. For example, in case of less treated concentration the coefficient K for leaves and stems are relatively similar during both times of observation, and only for roots the coefficient is much higher in case of growing miscanthus at the contaminated soil during 86 days. It has to be mentioned that results received for miscanthus growing at copper-contaminated soil may be discussed only relatively because the copper-content soil $CuSO_4 \times 5H_2O$ used for soil treatment is rather soluble in water and watering of miscanthus during time of experiment might impact the results.

4. Discussion of Results

These results can be compared to others in the literature. Kalembasa and Malinowska [9] also reported results with cobalt in which concentrations in miscanthus were small in some cases and not detected in other cases. All values were less than 1 mg/kg for plants irrigated with waste activated sludge. For copper, Kalembasa and Malinowka [9] reported concentrations in the range from 1.0 mg/kg to 5.3 mg/kg in miscanthus. Wilkins and Redstone [29] reported that the uptake of copper by miscanthus was similar for soils with significantly different concentrations. The concentrations in miscanthus ranged from 8 to 34 mg/kg for three different soils of 17 mg/kg, 188 mg/kg and 924 mg/kg of copper. For the two larger soil concentrations, the values of K are less than 10% and are generally smaller than the values in **Table 3** and **Table 4**.

Peng *et al*. [17] investigated copper uptake by 125 plant species and found that miscanthus has low uptake compared to most other plants. Results are reported for three sites in Southern China with copper concentrations in soil ranging from 43.8 to 228 mg/kg and copper concentrations in miscanthus ranging from 1.1 to 5.4 mg/kg. Values of K are less than 10%.

All of these results are in reasonable agreement. The value of K appears to be smaller for larger values of contaminant concentration in the soil, which indicates that miscanthus excludes cobalt and copper when concentrations in soil are large.

Iqbal *et al*. [8] reported that miscanthus reduced the availability of copper in soil compared to annual crops. The increase in organic carbon in the soil due to miscanthus growth and production is beneficial because of absorption of copper compounds, which reduces bioavailability.

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