Implementation of sustainable land management when using miscanthus for phytoremediation of soils contaminated by heavy metals

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CASEE, Zagreb, Croatia, July 1st,2013

Overview

- Advantages and disadvantages while using biofuels of second generation for phytoremediation
- Contamination of soils by heavy metals in Slovakia and Ukraine
- Methodology of the research
- Results obtained during first year of observation
- Discussions
- Summary

Advantages and disadvantages of Phytoremediation

- Phytoremediation is considered as environmentally friendly and forefront approach, essentially suitable for large sides' cleaning which have a relatively low levels of contamination
- Advantages: allows to treat contaminated cites without being excavated and transported, resulting in potentially cost savings
- Disadvantages: in situ treatment requires longer time periods, is uncertain in terms of uniformity of treatment because of variability of soils' or waters' characteristics, climate and other in-field conditions
- The time it takes to clean up a site depends on several factors:

✓ type and amounts of harmful chemicals present

✓ size and depth of the polluted area

✓ type of soil and conditions presentt

✓ type and number of plants being used

Using Biofuel plants for phytoremediation

Problems in regular phytoremediation process:

- ✓ Utilization of plants preliminary used for phytoremediation
- ✓ Increasing the price of the process during utilization the contaminated plants

Advantages of using biofuel crops for phytoremediation:

- ✓high productivity and production of large quantities of biomass
- ✓economic return can be obtained from the land transferring site

The use of food crops to produce biofuel of the first generation has met with concern because of the displacement of food crops and negative impact to the food security

Second generation biofuel crops which represented by not-food crops are less directly in conflict with food crops and would not effect the price of food

- Crops for second generation biofuel production can be divided into two main categories:

short rotation canopy species

perennial/ annual grasses

Poplar (Populus spp.)

Willow (Salix spp.)

Locust (Robinia spp.)

Switchgrass (Panicum virgatum L.)

Reed canary grass Phalaris arundinacea L.

Miscantus (Miscanthus sinensis A.., Miscanthus sacchariflorus M., Misaccantus x giganteus)

Research on Miscanthus for Phytoremediation of sites contaminated by heavy metals

While using miscanthus for two united processes: phytoremedian and second generation biofuel crops production the following important parameters have to be the subjects of research:

- impact of nature and concentration of contaminated substances
- kinetics of the process
- influence of agricultural conditions on crop growth
- Influence of agricultural conditions for phytoremediation effectiveness
- conditions of growing the second generation biofuel crops at the sites contaminated by heavy metals

Contamination by heavy metals

- There are 250.000 contaminated sites within European Union which require urgent attention (European Environmental Agency, 2009)
- In the US the number of Superfund sites is estimated as 1289 in 2011 (US Environmental Protection Agency, 2011) 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 (Report of the Ministry of Ecology and Natural Resources of Ukraine, 2012)
- In Slovakia large brownfields are at the former SU military places, the former mining production sites and relatively less contaminated sites are located at the agricultural regions which have smaller sizes (Report of Slovakian Ministry of the Environment, 2009)

The results of heavy metal determinations in the soils of Slovakia (mg/kg) (Kobza, 2005)*

Heavy metals	Total content***			Content in 2 mol/l HNO3****			Content in 0.05 mol/l EDTA		
	Geometric mean x_G	min	max	Geometric mean x_G	min	max	Geometric mean x_G	min	max
Cd	0.285	0.050	9.05	0.169	0.010	6.85	0.088	0.010	3.60
Pb	24.9	9.5	1050	14.2	3.70	649	3.56	0.160	268
Cr	72.7	10.5	170	2.09	0.100	43.1	0.162	0.010	2.90
Ni	12.8	0.3	57.5	3.22	0.200	19.1	1.04	0.110	8.60
Cu	22.3	5.0	156	7.55	1.00	171	3.27	0.300	80.5
Zn	64.3	11.0	1070	12.3	2.05	565	2.35	0.050	126
Hg	0.075	0.009	6.69	–	–	–	–	–	–

*altogether 429 sites were detected, among them 314 agricultural sites and 112 forestland sites**
** soil samples were collected from the surface layer (depth 0-0.1m) and treated
*** Total content was estimated after treatment of soil samples by mixture of acids ($HCl+HNO_3+HF$)
**** EPA standard

Monitoring site*	Dimensionless concentration of metal based on annual average /dimensionless maximum value**					
	Cd	Mn	Cu	Ni	Pb	Zn
Mariupol'	0.2/1.0	1.4/3.7	1.3/5.4	0.3/0.6	3.7/20.4	2.1/4.6
Dnipropetrovsk	1.1/3.0	1.0/4.1	0.8/6.9	0.2/0.5	1.5/22.7	0.4/0.7
Kyiv	0.8/5.7	0.2/0.6	0.5/1.8	0.2/0.5	1.2/4.6	1.2/4.4
Fastiv, Kyiv oblast	0.3/1.6	0.3/0.6	0.7/3.0	0.2/0.9	3.9/19.8	1.5/4.6
Bila Tserkva, Kyiv oblast	0.0/0.3	0.3/0.6	0.2/1.1	0.2/0.4	1.1/8.6	0.9/3.1
Yalta	0.1/0.5	0.7/2.8	1.6/13.5	0.5/1.2	2.1/11.7	0.9/5.7
Lutsk	0.1/0.5	0.3/0.4	0.6/5.6	0.2/1.0	0.6/6.3	1.1/3.8
Khmelnytskyi	0.0/0.3	0.5/0.9	0.6/4.7	0.4/0.8	1.4/6.5	1.1/3.3
Chernihiv	0.0/0.0	0.2/0.6	0.1/0.6	0.1/0.4	0.5/3.8	0.3/0.9

* Spelling are Ukrainian in accordance with http://www.mapofukraine.net/travel_info/list-of-ukrainian-cities-and-towns.html; oblast is a geographic region

**Measured concentration in selected sites relative to average concentration in soils and maximum values relative to average concentration, dimensionless

Виробники бутильованої води в Україні

№	Марка	Виробник/Місце видобування води
1	BonAqua	«Coca Cola Беверидж Україна Лімітед», Київська обл., смт Велика Димерка
2	Clear Water	ТОВ «Чиста вода», Київська обл., с. Мила
3	Анжей	ПП «Завод продтоварів «Анжей», Луганська обл., Лутугинський р-н, с. Георгіївка
4	Березівська	ВАТ «Березівські мінеральні води», Харківська обл., с. Березівське
5	Біола Знаменська	ЗАТ «Ерлан», Дніпропетровська обл., м. Підгорне
6	Бон Буассон	ПП «Агентство Мальбі», м. Дніпропетровськ
7	Голубий ключ	ТОВ «Мілеміум», м. Луганськ
8	Дніпропетровська	АТЗТ «Новомосковський Завод Мінводи», Дніпропетровська обл., с. Знаменка
9	Золотий колодязь	ЗАТ «Золотий колодязь», Донецька обл., м. Білозірське
10	Іллічівська	ВАТ «Маріупольський металургійний комбінат ім. Ілліча», м. Маріуполь
11	Карпатська джерельна	ТОВ «Карпатські мінеральні води», Львівська обл., м. Струтин
12	Кримська	СП «Кримські води ЛТД», м. Сімферополь
13	Кришталева гірська	ПП «Віктар», Львівська обл., м. Бережани
14	Кула	ЗАТ «Кула-Крим», Херсонська обл., с. Ісходнює
15	Моршинська	ВАТ «Моршинський завод мінеральних вод «Оскар», Львівська обл., м. Моршин
16	Надбручанська	ПП «Батіг», Тернопільська обл., смт. Гусятин
17	Оболонська	ЗАТ «Оболонь», м. Київ
18	Ордана	ЗАТ НПЦ «Ордана», м. Київ
19	Полтавські джерела	ТОВ «Світанок», м. Полтава
20	Романівська	ТОВ ВЕФ «Аква-Віта», м. Донецьк
21	Софія Київська	Київський завод безалкогольних напоїв «Росинка», м. Київ
22	Союз	ПП «Союз-ТМ», м. Донецьк
23	Старий Миргород	ЗАТ «Миргородський завод мінеральних вод», м. Миргород
24	Трускавецька Заповідна	ПТВФ «Анна-Г», Львівська обл., м. Дрогобич
25	Трускавецька Кришталева	ТзОВ «Аквар'юс», Львівська обл., м. Трускавець
26	Цілюща	ТОВ «Техводсервіс», м. Київ
27	Шаянська джерельна	ТОВ «Шаянські мінеральні води», Закарпатська обл., смт Вишково
28	Еден	ТОВ «Райські Джерела», Київська обл., с. Таценки
29	Еталон	ТОВ «Субос-Україна», м. Київ

Research places in Ukraine,2013

Soil contamination by heavy metals, Kamenetz-Podilsky, Ukraine

Number of test	Depth of test taking (cm)	Weight for test, (г)	Volume of extracted test, (ml)	Concentration of heavy metals (mg/kg)					
				Cu	Zn	Co	Mn	Cd	Pb
P1	0-30	10	50	1,31	9,26	2,43	**151,6**	0,37	**9,74**
	31-60	10	50	1,63	10,5	**4,38**	**337,0**	0,36	**20,6**
	61-90	10	50	1,11	5,29	1,64	**141,7**	0,41	**7,38**
P2	0-30	10	50	1,09	4,25	3,47	**268,8**	0,20	**10,5**
	31-60	10	50	1,49	5,24	3,53	**351,0**	0,50	**10,7**
	61-90	10	50	1,22	5,24	3,94	**517,7**	0,28	**8,58**
P3	0-30	10	50	0,88	2,70	1,32	139,3	0,32	**6,87**
	31-60	10	50	0,73	0,85	1,09	26,9	0,30	3,73
	61-90	10	50	1,11	1,18	2,10	115,6	0,44	**6,28**
Limited concentration of metals in the soil (mg/kg)				**3,0**	**23,0**	**5,0**	**140,0**	**0,6**	**6,0**

Research on using second generation biofuels for phytoremediation

- To research the behavior of selected metals (cobalt and copper) at the soil preliminary artificially contaminated by metals (in a form of substances: $CuSO_4$ and $CoCl_2$
- To explore the dynamic of the process (32 days and 86 days)
- To evaluate the differences between behavior of copper and cobalt

Cobalt and cupper were used in the form of solution, respectably, $CoCl_2 \times n H_2O$ or $CuSO_4 \times 5 H_2O$ with concentration 200 mg/l, 400 mg/l and 800 mg/l

Conditions of the Research

- Evaluation of Cu/Co in the plants' parts were done by using **Spectrometer AAS AVANTA ∑ by GBC Scientific with the** electrothermal atomization. Autosampler PAL 3000 was used for electrothermal analysis. Analysis and results' evaluation were supported by software GBC Avanta ver.2.0
- Soil used had a standard characteristics: Total nitrogen (in a form of N) content (% max) -1.9
  - Total phosphorus content (in a form of P2 05) (%max) -0,5
  - Total potassium content (in a form of K20) (% max) – 0,7
  - pH – 4.5-6.0
  - electrical conductivity (mS/cm) – 0,8
  - humidity (%max) -65

Concentration of Co in miscanthus plants after 32 days of soils' treatment by solution of $CoCl_2 nH_20$

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		
12,58	ND*	ND	ND	-	ND	ND	ND	-	ND	ND	ND	-
25,16	ND	ND	ND	-	ND	ND	ND	-	ND	ND	ND	-
50,32	0,43	0,62	0,525	1,04	ND	ND	ND	-	0.03	ND	0,03	0,05

Concentration of Co in miscanthus plants after 86 days of soils' treatment by solution of $CoCl_2 nH_2O$

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		
12,58	ND	ND	ND	-	ND	ND	ND	-	ND	ND	ND	-
25,16	0,44	0,62	0,53	2,1	ND	ND	ND	-	ND	ND	ND	-
50,32	0,84	0,81	0,825	1,64	0,05	ND	0,05	0,09	0,02	ND	0,02	0,04

Concentration of Cu in miscanthus plants after 32 days of soils' treatment by solution of $CuSO_4 x5 H_20$

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		
22,10	2,40	3,60	3,00	13,57	1,20	2,20	1,70	7,69	2,10	2,00	2,05	9,28
44,20	7,20	4,60	5,90	13,35	1,00	2,00	1,50	3.39	3,20	7,20	5,20	11.76

Concentration of Cu in miscanthus plants after 86 days of soils' treatment by solution of $CuSO_4$ x5 H_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		
22,10	7,40	No data	7,40	33,4	1,00	2,40	1,70	7,69	2,60	2,00	2,30	10,40
44,20	6,30	10,20	8,25	18,66	5,00	7,20	6,10	13,8	6,80	7,40	7,10	16,06

Conclusion

- The obtained results showed relatively bigger undertaken of cupper in comparison with cobalt by miscanthus
- The highest concentration of cupper was detected in the roots and smaller concentrations were in staves and leaves during all monitored time.
- Cobalt was detected only for highest treated concentration of metal and only in the roots
- Miscanthus biomass received at cobalt contaminated soil may be used for energy production because the above surface part accumulated only limited traces of the metal and fit the requests

Thank you for the attention!

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