Ecotoxicity of Pyrolytic Carbon Produced by Pyrolysis of Municipal and Industrial Waste

Jana ČERNECKÁ[1], Hana ŠKROBÁNKOVÁ[2] Helena RACLAVSKÁ[3], Kateřina HELIOVÁ[4], Michaela BENDOVÁ[5]

[1] VSB – Technical University of Ostrava, Faculty of Mining and Geology, 17. listopadu Str. 15, Ostrava-Poruba, Czech Republic; email: jana.cernecka@vsb.cz
[2] VSB – Technical University of Ostrava, Faculty of Mining and Geology, 17. listopadu Str. 15, Ostrava-Poruba, Czech Republic; email: hana.skrobankova@vsb.cz
[3] VSB – Technical University of Ostrava, Faculty of Mining and Geology, 17. listopadu Str. 15, Ostrava-Poruba, Czech Republic; email: helena.raclavska@vsb.cz
[4] VSB – Technical University of Ostrava, Faculty of Mining and Geology, 17. listopadu Str. 15, Ostrava-Poruba, Czech Republic; email: katerina.heliova.st@vsb.cz
[5] VSB – Technical University of Ostrava, Faculty of Mining and Geology, 17. listopadu Str. 15, Ostrava-Poruba, Czech Republic; email: michaela.bendova@vsb.cz

DOI: 10.29227/IM-2017-01-20

Abstract

The samples of pyrolytic carbon from Burgau Waste Pyrolysis Plant (Germany) produced by pyrolysis of municipal, industrial and special waste were monitored in terms of ecotoxicity. Collembola *(springtails) were selected for reproductive bioassay. After 28 days' incubation of juveniles, the value of* EC_{50} *was determined for selected metals. The study indicates the lowest sensitivity of* Folsomia candid*a to iron (1.689 mg/kg dry matter correspond to* EC_{50}*). The relative sensitivity for other metals can be expressed in form of a series:* $Fe < Zn = Cu < Pb < Mn < Ni = Cd$*. The highest sensitivity was found for cadmium (1.2 mg/kg dry matter). Pyrolytic carbon from MPA Burgau contains high concentrations of chlorides, which cause inhibition of reproduction of* Folsomia candid*a and therefore represent a limiting factor for determination of ecotoxicity of heavy metals in* Folsomia candid*a. The index of acute toxicity* EC_{50} *was obtained for concentration of 500 mg/kg chlorides in dry matter.*

Keywords: biochar, pyrolytic carbon, Collembola*, heavy metals, ecotoxicity, inhibition of reproduction*

Introduction

One of the pyrolysis products is pyrolytic carbon (PC) – char; intensive search for its utilization is going on. Pyrolytic carbon can be used as a sorbent in power engineering, or in the case of pyrolysis of biomass, biochar is formed, which can be used for agricultural purposes.

Biochar is defined as a product with a high content of carbon produced by heating biomass in a closed space with little or no air accession (Lehmann and Joseph, 2009). Biochar application in soil has mainly environmental and agricultural benefits. Currently, biochar is added to soil in order to improve its fertility or function (Laird et al., 2010). Its addition to the soil affects the value of the acid-base reaction, it makes it possible to maintain or increase the supply of nutrients, it increases the water holding capacity of soil, reduces the mobility of heavy metals and organic pollutants. Raw material composition and pyrolysis technology affects the quality of the resulting biochar (Di Blasi, 2008; Harder and Forton, 2007). Biochar added to the soil to improve the soil properties has to meet the requirements defined in the International Biochar Initiative (IBI, 2016 Standardized Product Definition and Product Testing Guidelines for Biochar That is Used in Soil).

Potential negative impacts on soil biota may be caused by excessive salinization or release of pollutants from biochar (McCormack et al., 2013; Liesch et al., 2010). Standard IBI Biochar contains limit values for physical and chemical parameters, limits for contaminants (BTEX, PAHs, PCBs, PCDD/PCDF and metals). For the environmental risk assessment of biochar, ecotoxicity is used (Brock, 2013). IBI Biochar Standard includes only tests for germinating seeds and earthworms (IBI, 2016). Selecting an organism to determine the ecotoxicity is still debated. Currently, the research on biochar is going on in terms of the appropriateness of the test organism selection (Busch et al. 2013; Domene et al. 2015; Hale et al. 2013; Marks et al. 2014; Rogovska et al. 2012).

Ecotoxicity of pyrolysis carbon formed from materials other than biomass should be monitored through the elimination of hazardous properties in the assessment of waste (Decree on the evaluation of hazardous waste properties 94/2016 Coll.).

Aim of this paper is to evaluate ecotoxicity monitored by the reproductive test for *Folsomia candida* organism and evaluation of the causes for inhibition. For testing, pyrolytic carbon was selected containing high concentrations of metals, which may be involved in the inhibition of *Folsomia candida*.

Tab. 1 Results of chemical analysis of pyrolysis carbon from Burgau

Tab. 1 Wyniki analizy chemicznej karbonizatu z Burgau

Element	Ca	Si	Cl	Al	Fe	K	Mg	Ti	S	P	
Concentration (% dry matter)	8.44	4.79	2.8	1.21	0.98	0.5	0.51	0.38	0.28	0.12	
Element	Zn	Ba	Cu	Pb	Mn	Sn	Cr	Br	Sb	Ni	Cd
Concentration (mg/kg dry matter)	3,120	1,290	933	677	570	373	177	107	88.3	23.2	8.3

Tab. 2 Chemical analysis of particle with high content of Sn (wt. %)

Tab. 2 Analiza chemiczna ziarna o wysokiej zawartości Sn (%)

	Analysed point						
Element	1	2	3	4	5	6	7
C	10.18	3.24	5.4	11.54	6.48	3.6	
O	16.73	6.9	14.7	16.95	12.64	4.19	
Al	0.25	0.84	0.66		1.9	0.66	
Si	0.86	0.68	0.68		0.71	0.88	1.31
Pb	2.66	3.99	6.39			16.65	
Cl	3.1		4.76	9.36	13.38		10.3
Sn	63.68	75.84	66.62	4.41	62.45	72.25	82.67
Ca	2.63			0.45			2.93
Cu		2.95					0.71
Zn		5.55		57.28	3.22	1.76	
Na			0.79				0.88
S							1.38

Materials and methods

The material used to research inhibition of *Folsomia candida* was pyrolytic carbon obtained from MPA Burgau, 2.2 MWe waste pyrolysis plant in Günzburg, Bavaria. The Burgau plant utilizes 35,000 tons per year of urban, industrial and special waste through pyrolysis two cylinders. Waste pyrolysis takes place at the temperature of about 450–500°C. Organic substances are thermally decomposed and form gaseous combustibles (pyrolysis gas) and a solid one (pyrolysis coke/carbon). In late 2015, MPA Burgau was closed due to the high economic costs of operation and difficulties in dealing with pyrolytic carbon (hazardous waste).

Chemical composition of pyrolytic carbon from MPA BURGAU was analysed by X-ray fluorescence in the Public Health Institute in Ostrava (ZUOVA). The determination of the ash content was performed according to ČSN (Czech National Standard) ISO 602, and the volatile matter in accordance with ČSN ISO 562 "Black coal and coke". The mineralogical composition of pyrolytic carbon (hereinafter referred to as PC) was determined by X-ray diffraction using Bruker-AXS D8 Advance diffractometer, measurement geometry theta/2 theta, semiconductor detector LynxEye (VŠB-TU Ostrava, ICT). To determine the effect of risk elements for ecotoxicity, it is necessary to know the forms of the occurrence of metals. For this reason, PC samples were used to prepare a polished section, which was examined using scanning electron microscopy (SEM, FEI Quanta 650 FEG) with the analysis using energy dispersive analyser EDAX. Aqueous extract 1:10 was prepared from the PC sample according to Decree No. 294/205 Coll.

PC ecotoxicity test was performed on *Collembola*, specifically for inhibition of reproduction of *Folsomia candida*. *Collembola* are considered one of the most important test organisms at all; they can indicate possible impacts of biochar on soil biota. *Collembola* were prepared in accordance with ISO 11267 (ISO 2014 Soil quality – Inhibition of reproduction of *Collembola* (*Folsomia candida*) by soil contaminants). Inhibition was determined in eight repeating tests, which were carried out in 100 ml beakers with 30 g of wet weight of soil. The soil was mixed with PC so that PC corresponded the addition of 0; 0.5; 1.0; 2.5; 5.0; 10.0; 15.0; 20.0%. For biological tests, 10 to 11 days old *Collembola* were used, the so-called juveniles; they were always in a group of 10 pieces. The moistened mixture was incubated for 28 days under low light conditions and at a temperature of 20 ± 2°C. It was also necessary to aerate the mixture and feed the individuals with brewer's yeast. At the end of the test, the samples were

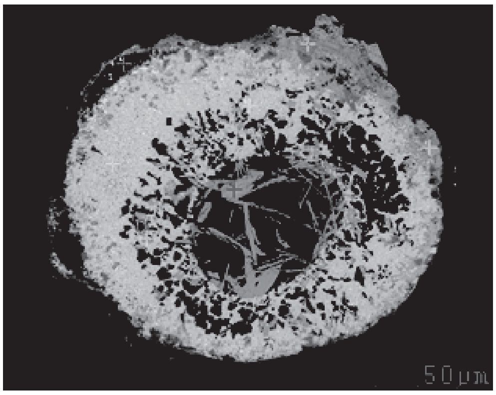

Fig. 1 Scanning electron microphotograph of the particle with high content of Sn and analysed points

Rys. 1 Obraz z elektronowego mikroskopu skaningowego ziarna o wysokiej zawartości Sn

placed in Petri dishes and diluted with water, so that the individuals swam on the surface. Subsequently, images were shot for counting the number of adults and new juveniles. Reproduction was calculated using ImageJ – Executable Jar File software. For each concentration, the arithmetic average of the dead or the surviving individuals was calculated from all determinations. The mortality rate percentage is calculated against the original 10 individuals based on an average of the individual concentrations, or inhibition of reproduction. The resulting EC_{50} values (mortality or inhibition of 50% of individuals) were determined from the dependence between inhibition and metal concentration in the substrate.

Results and discussion

The results of chemical analysis using X-ray fluorescence are shown in Table 1. Pyrolytic carbon contained 61% of ash, 21% of volatile combustible, and 18 % of fixed carbon, the calorific value was 9.14 MJ/kg. The high ash content is one of the reasons why this material is not suitable for energy use. Pyrolytic carbon has high contents of Zn, Cu, Pb, and Sn. Ash in pyrolytic carbon contains three crystalline phases: quartz (3.09%), calcite (7.24%) and cordierite $(Mg, Fe)_2Al_3(AlSi_5O_{18})$ – cyclosilicate 2.56%.

Since the mechanism of interaction of metals and a method of affecting *Folsomia candida* is not entirely clear, the form of occurrence of metals was determined using SEM with energy dispersive analyser. The toxicity of pollutants depends on the sensitivity of the test organism, but also on the properties of the matrix which regulates bioavailability of pollutants. Bioavailability is explained as sorption equilibrium between the solid phase (sludge, soil) and interstitial water. Domene et. al. (2010) states that interstitial water is the main medium that carries pollutants affecting springtails, while transmission through the solid matrix is minimal. The toxicity of the environment for some soil organisms and aquatic organisms is due to soluble components (Domene et. al., 2010).

The results of microanalysis show that pyrolysis carbon comprises particles having a high content of Sn, which ranges from 4 to 75% (Table 2). Fig.1 shows scanning electron microphotograph of the particle with analysed points. Tin is present predominantly in the form of chlorides. Furthermore, there are metallic particles with a high content of Cu-Zn or Cu-Pb, or possibly ZnCl2, and metal particles of Pb-Zn with Pb content of about 80%. Metal particles of Pb-Sn contain 60 to 70% of Pb. Due to the occurrence of metal in the form of metallic phases, their leachability is minimal (Table 3). The critical parameter in an aqueous extract are dissolved substances reaching a concentration of 10–11.5 g/L and exceed the limit (8 g/L) for evaluating the hazardous property H15 (Decree 94/2016 Coll.) The high content of dissolved substances in the extract is due to chlorides amounting to about 48%, sulphates amounting to 8%, and also cations (Table 3).

Inhibition of reproduction of *Folsomia candida* is also reflected in artificial soil without the addition of pyrolytic carbon, and up to 10% addition of pyrolytic carbon, inhibition of reproduction is comparable to that obtained for the soil without the addition of PC. A significant increase in inhibition, which is higher than 30%, was obtained after the addition of 15% of pyrolysis carbon (Table 4). From the curve of inhibition, EC_{50} value was calculated, which corresponds to 18% of added pyrolytic carbon (Fig. 2).

In pyrolytic carbon, the highest concentration was found for Zn (0.3%). Influence of Zn on reproduction of *Folsomia candida* was studied by Lock and Janssen (2003). They found that Zn in various forms of the occurrence affects reproduction of *Folsomia candida* in varying degrees. The smallest influence was found for metallic Zn, and also for ZnO, the highest influence on reproduction was found for salts of Zn, which is influenced by their solubility. Acute toxicity was not found,

Tab. 3 Leachability of pyrolytic carbon

Tab. 3 Podatność na ługowanie karbonizatu

Leachates		Pyrolytic carbon			
		1 hour	24 hours	2 hours	4 hours
Conductivity	[µS/cm]	14,500	14,410	14,930	15,590
Dissolved substances	[mg/L]	10,240	10,185	11,360	11,580
Cl^{-1}		4,372	4,408	4,620	4,878
$(NO_2)^-$		DL	DL	DL	DL
$(NO_3)^-$		6.087	6.069	6.16	5.94
$(NH_4)^+$		0.46	0.52	0.331	0.157
$(PO_4)^{3-}$		7.957	7.949	33.53	9.01
$(SO_4)^{2-}$		832.40	854.71	1000.14	1080.44
P		8.00	8.01	0.12	0.06
K^+		2,140	1,886	2,046	2,111
Zn	[µg/L]	4.7	4.1	1.2	< 1.0
Cu		1.7	1.5	1.2	< 1.0
Pb		14.1	13.2	14.2	14.5
pH		9.14	8.95	7.22	7.53
TOC	[mg/L]	46.28	47.56	48.94	47.38

Tab. 4 Reproduction inhibition in *Folsomia candida* (mean from 8 experiments) in %

Tab. 4 Zahamowanie rozmnażania *Folsomia candida* (średnia z ośmiu eksperymentów) [%]

Added PC	0	0.5	1	2.5	5	10	15	20
Mean	21.83	20.49	19.02	16.91	19.56	24.59	34.43	62.38
Standard deviation	16.29	17.47	14.17	10.69	17.53	14.09	18.13	21.48

Tab. 5 Concentration of metals corresponding to the index of acute toxicity (EC_{50}) for *Folsomia candida*

Tab. 5 Stężenie metali w relacji do wskaźnika toksyczności ostrej (EC_{50}) dla *Folsomia candida*

Element	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Sb	Sn	Zn	Cl
Concentration (mg/kg dry matter)	1.2	3.5	167	1,689	102.1	4	121	16	65.5	167	500

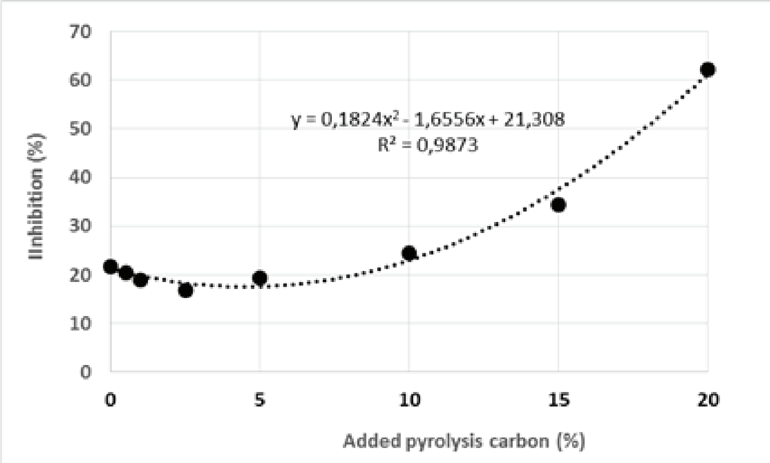

Fig. 2 Polynomial correlation between inhibition of reproduction of *Folsomia candida* and the amount of pyrolytic carbon added to the soil (%)

Rys. 2 Korelacja wielomianowa pomiędzy zahamowaniem rozmnażania *Folsomia candida* oraz ilością karbonizatu dodanego do gleby (%)

not even at the Zn concentration of 3,200 mg/kg of dry matter. The study confirmed that for Zn, acute toxicity is influenced by the metal concentration in soil water (dermal transfer), but also through the food, which is also a significant way.

The values of the growth inhibition in *Folsomia candida* and calculated concentrations of metals (based on the addition of pyrolytic carbon into the soil), the concentration value that specifies the index of acute toxicity EC_{50} was calculated (Table 5).

Reproduction of *Folsomia candida* is significantly affected at a NaCl concentration of 0.7 g/kg and conductivity of 493 µS/cm; from these concentrations, reproduction continuously decreases (Pereira et al., 2015). In the case of PC Burgau, conductivity was measured significantly about 30 times higher (14,500 to 15,590 µS/cm). Higher sensitivity of *Collembola* while increasing conductivity over the value of 1030 µS/cm is stated by Owojori et al. (2014). Similar results were obtained for the reduction of reproduction of *Folsomia candida* – the value of EC_{50} for chlorides in the aqueous matrix 500 mg/L and conductivity of 2000 µS/cm.

Conclusion

The value of 30% for inhibition of reproduction of in *Collembola* was achieved when adding 12.4% of pyrolysis carbon. Inhibition is not caused by metals present in pyrolytic carbon, because metals pass into the water-soluble form in a concentration of up to µg/l. The lowest sensitivity to contents of elements in pyrolytic carbon for *Folsomia candida* (within testing EC_{50}) was found for the metals in the order: Fe < Zn = Cu < Pb < Mn < Ni = Cd. Inhibition of reproduction of *Folsomia candida* is caused by high concentrations of dissolved substances, especially chlorides. The index of acute toxicity EC_{50} was obtained for a concentration of 0.5 g/kg of chlorides in the dry matter.

Acknowledgements

This paper was supported by research projects of the Ministry of Education, Youth and Sport of the Czech Republic: The National Programme for Sustainability LO1404 – TUCENET and SP2016/31 “Optimization of compost properties with addition of biochar”.

Literatura – References

1. BROCK, Theo M. Priorities to improve the ecological risk assessment and management for pesticides in surface water. Integrated Environmental Assessment and Management, 9, 2013, p. 64-74.
2. BUSH, Daniela et al. Genotoxic and phytotoxic risk assessment of fresh and treated hydrochar from hydrothermal carbonization compared to biochar from pyrolysis. Ecotoxicology and Environmental Safety, vol. 97, 2013, p. 59–66.

3. DI BLASSI, Colomba. Modeling chemical and physical processes of wood and biomass pyrolysis. Progress in Energy and Combustiton Science, 34(1), 2008, p. 47–90.
4. DOMENE, Xavier et al. Ecotoxicological characterization of biochar: Role of feedstock and pyrolysis temperature. Science of The Total Environment, 512-513, 2015, p. 552–561.
5. HALE, Sarah E. et al. Short-term effect of the soil amendments activated carbon, biochar, and ferric oxyhydroxide on bacteria and invertebrates. Environmental Science and Technology, 47(15), 2013, p. 8674–8683.
6. HARDER, Marie K. and FORTON, Oatric Tening. A critical review of developments in the pyrolysis of automotive shredder residue. Journal of Analytic and Applied Pyrolysis, 79(1-2), 2007, p. 287–394.
7. INTERNATIONAL BIOCHAR INITIATIVE. Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in Soil, 2016.
8. LAIRD, David et al. Biochar impact on nutrient leaching from a Midwest agricultural soil. Geoderma, 1158(3-4), 2010, p. 436–442.
9. LEHMANN, Johannes and JOSEPH, Stephen. Biochar for environmental management: science and technology. 1st edition. Sterling, VA: Earthscan, 2009, XXXII, p. 416, ISBN 18-440-7658-X.
10. LIESCH, Amanda M. et al. Impact of two different biochars on earthworm growth and survival. Annals of Environmental Science, 4, 2010, p. 1–9.
11. LOCK, Koen and JANSSEN, Colin R. Comparative toxicity of a zinc salt, zinc powder and zinc oxide to Eisenia fetida, Enchytraeus albidus and Folsomia candida. Chemosphere, 53 (8), 2003, p. 853–856.
12. MARKS, Evan A. N. et al. Biochars provoke diverse soil mesofauna reproductive responses inlaboratory bioassays. European Journal of Soil Biology, 60, 2014, p. 104–111.
13. MCCORMAC, Sarah A. et al. Biochar in bioenergy cropping systems: Impacts on soil faunal communities and linked ecosystem processes. GCB Bioenergy, 5(2), 2013, p. 81–95.
14. OWOJORI, Olugbenga J. et al. Comparative study of the effects of salinity on life-cycle parameters of four soil-dwelling species (Folsomia candida, Enchytraeus doerjesi, Eisenia fetida and Aporrectodea caliginosa). Pedobiologia, 52, 2008, p. 351–360.
15. PEREIRA, Carla S. et al. Effect of NaCl and seawater induced dalinity on survival and reproduction of three soil invertebrate species. Chemosphere, 135, 2015, p. 116–122.
16. ROGOVSKA, Natalia et al. Germination tests for assessing biochar quality. Journal of Environmental Quality, 41(4), 2012, p. 1014–1022.

Ekotoksyczność karbonizatu z pirolizy odpadów komunalnych i przemysłowych

Próbki karbonizatu z Burgau Waste Pyrolysis Plant (Niemcy) wytwarzanego podczas pirolizy odpadów komunalnych, przemysłowych i specjalnych były badane pod kątem ekotoksyczności. Do badań biologicznych rozmnażania wybrano Collembola *(skoczogonki). Po 28 dniach inkubacji młodych, ustalono wartość EC_{50} dla wybranych metali. Badanie wykazało najniższą wrażliwość* Folsomia candida *na żelazo (1,689 mg/kg suchej masy w stosunku do EC_{50}). Relatywna wrażliwość na inne metale może zostać zaprezentowana jako Fe < Zn = Cu < Pb < Mn < Ni = Cd. Najwyższą wrażliwość stwierdzono dla kadmu (1,2 mg/kg suchej masy). Karbonizat z MPA Burgau zawiera wysokie stężenia chlorków, które powodują zahamowanie reprodukcji Folsomia candida a zatem jest ograniczonym wskaźnikiem ekotoksyczności metali ciężkich. Wskaźnik toksyczności ostrej EC_{50} otrzymano dla stężenia 500 mg/kg chlorków w suchej masie.*

Słowa klucze: biowęgiel, karbonizat, Collembola*, metale ciężkie, ekotoksyczność, zahamowanie rozmnażania*