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Chemical and ecotoxicological evaluation of biochar produced from residues of biogas production

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HIGHLIGHTS

- Biochars produced at different temperatures from biogas residue (RBP) were evaluated.
- Biochars fulfilled recommendation regarding to heavy metals and PAH.
- Biochars from non-separated RBP were the most toxic for investigated organisms.
- Biochars from separated, mesophilic RBP characterized the most favorable properties.
- Biochars produced at 800 °C presented unfavorable conditions for plants and arthropod.

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ABSTRACT

Analyses were carried out for biochars produced at three temperatures of pyrolysis (400, 600 and 800 °C) from solid residue from biogas production (RBP). Separated and non-separated RBP from biogas plants employing different biogas production conditions were pyrolyzed. The contents of heavy metals and polycyclic aromatic hydrocarbons (PAHs) (16 PAH US EPA) were analyzed in biochars. The analyses showed that with an increased pyrolysis temperature, there was an increase in the contents of PAHs and of certain heavy metals (Cr, Cu, Cd, Pb and Mn). In the ecotoxicological tests, it was noted that the effect depended on the temperature of pyrolysis and on the feedstock from which the biochar was produced. The least harmful effect on the test organisms was from biochar produced by separated RBP in a biogas plant operating in mesophilic conditions. The most negative effect on the test organisms was characteristic of biochar produced from non-separated mesophilic RBP. This study shows that the main factors determining the level of toxicity of biochars produced from RBP towards various living organisms are both the method of feedstock production and the temperature at which the process of pyrolysis is conducted.

1. Introduction

The most frequently used raw materials for biogas production are mainly agricultural and food waste, animal feces and sewage sludge [1]. In the process of fermentation, those materials are used in various proportions and at various temperatures (mesophilic, thermophilic) [2]. Apart from biogas, another product of this anaerobic fermentation is the post-fermentation digestate (RBP), which is often separated into liquid and solid phases [1]. RBP can be composted, or landfilled, but most often it is used as a fertilizer in agriculture. However, research shows that the direct application of RBP to soils may be limited not only because it may contain heavy metals, polycyclic aromatic hydrocarbons (PAH) [3], seeds of weeds or infrequent parasites [2] but also because of the high mobility of its nutrients [4], which causes leaching of the nutrients from the soils and increases the eutrophication of water. Given the drawbacks of deriving fertilizer from RBP, the conversion of RBP into biochar, a popular alternative in recent years, may be an interesting solution. An effect of RBP conversion into biochar is the immobilization of organic carbon and nutrients in soil [5,6]. Additional advantages of the use of biochar is an increase in crop yields, the limitation of nutrient leaching [5] and the reduction of bioavailability of heavy metals and PAHs, which are present in feedstock and soil [7].

An increase in the production of biochars from waste materials requires an in-depth analysis of their properties in the context not only of the potential benefits but also of the potential threats to the environment. Apart from the estimation of the contami-

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Table 1
Characterization of biogas production plants.

Location	Type of fermentation	Efficiency of biogas (mln m^3/year)	Feedstocks	Fraction of RBP	Sample ID
Uhnin	thermophilic	4.5	maize silage 55%. straw 15%. sugare bagasse beet 15%. pumace of fruit 10%. manure 5%	Separated	UHS
Koczergi	mesophilic	3.9	maize silage 60%. potato pulp 15%. distillers grains 10%. sugare bagasse beet 10%. manure 5%	Separated	KOS
Piaski	mesophilic	3.9	maize silage 65%. sugare bagasse beet 15%. pumace of fruit 10%. wastes from dairy 5%. manure 5%	Non-separated	PI

Table 2
Trace metal content (mg/kg) in biochars produced from RBP.

Biochars	Temperature of pyrolysis [°C]	Cr	Zn	Ni	Cu	Mn	Cd	Pb
BCUHS	400	29.2	168	10.0	28.7	452	3.6	3.3
	600	29.8	137	30.6	33.9	458	3.8	3.4
	800	19.0	22	12.0	31.4	484	4.1	3.7
BCKOS	400	4.2	76.7	<DL	20.4	128	8.1	23.8
	600	10.3	121	20.9	29.9	181	8.7	25.1
	800	29.3	13.3	6.6	29.3	260	8.6	25.9
BCPI	400	35.4	132	10.9	58.0	169	1.9	12.1
	600	28.2	301	33.6	77.7	242	2.4	12.6
	800	38.9	40	17.3	67.6	237	2.3	12.7

nant content, such as heavy metals or PAHs, in biochars, it is also important to determine how biochar added to soil will affect living soil organisms. Recent studies show [8–10] that in spite of their acceptable content of contaminants, biochars may have an adverse effect on living organisms. In light of the information given above, a strict control of biochars appears to be necessary. Biochars should not be applied to soils without prior characterization comprising the physicochemical analyses, content of contaminants and effects on organisms. Permissible content of different pollutants such as heavy metals or PAHs in sewage sludge or composted organic waste (which may be used as a fertilizer) are strictly defined and respected in most countries. The situation is different in the case of RBP, for which there is lack of legal regulations. The exception is Switzerland where the amount of PAHs in RBP is clearly specified. The same is the case with biochar. Only in Switzerland, the European Biochar Certificate (voluntary industry standard in Europe) is obligatory for the use of biochar in agriculture. This regulation concerns the properties and permissible content of different contaminants in biochar [11].

RBP is a specific material, and due to its increasing production may be interesting to use for the biochar production. Previous studies have shown [12] that biochar produced from RBP can have better properties than the original RBP, but there is no information about the environmental risks associated with its use.

The objective of this study was to determine the content of PAHs, heavy metals, and of the level of toxicity of biochars produced from RBP at various temperatures towards various groups of organisms. The study was conducted with the use of RBP acquired from three different biogas plants operating under various production regimes. This study may prove that biochar produced from RBP may have better properties for agricultural use and be less toxic than the RBP itself. This is particularly important considering insufficient studies that have been reported for this type of material.

2. Materials and methods

2.1. Biochar preparation

Three different residues from biogas production were used in the present study. The biogas plants mainly differed in the type of the process temperature (mesophilic: 32–37 °C, thermophilic: 52–55 °C) and the separation at the solid and liquid fractions (Table 1). RBP was collected during spring 2014 after the fermentation process of the pipeline drain in the case of liquid fraction and separator; this is the solid fraction. The samples were mixed, dried at 30–35 °C for approximately 10 days (solid phase) or 30 days (non-separated phase), ground in a mortar ceramic and passed through a 2 mm sieve. Detailed information about RBP pyrolysis is presented in the supplementary information (SI).

2.2. Trace metals and polycyclic aromatic hydrocarbons determination

The total metal concentration was determined using a PROLABO microwave oven (Microdigest 3.6, France) via a wet method in a mixture of 65% nitric acid (8 ml) and 70% perchloric acid (8 ml) at a ratio of 1:1. A 30% hydrogen peroxide solution was added before the acid. Analysis of the Cr, Cu, Ni, Mn, Pb, Cd and Zn contents was carried out using emission spectrometry on ICP-OES (Leeman, Labs, PS 950). Evaluation of the accuracy and precision of the analytical procedures used reference materials (Heavy Clay Soil, RTH 953. Promochem).

PAHs were extracted by the Soxhlet method. The extracts were washed (using DMF/hexane [13] and an open micro glass column [9]) and evaporated to 0.5 ml. The final concentrated extracts were analyzed using gas chromatography (Trace 1300) mass spectrometry (ISQ LT) (GC–MS, Thermo Scientific). Detailed information about the extraction, washing and PAH GC–MS analysis is presented in the supporting information.

2.3. Biochar toxicity

Biochar (BC) samples were evaluated by solid phase (Collembolan test, Phytotoxkit F) and liquid phase tests (Microtox®, Phytotestkit F).

To evaluate biochar toxicity to springtails (Collembolan test), the test was carried out with *Folsomia candida* according to ISO guideline 11267 [14]. To evaluate the effect of biochar on plants, the Phytotoxkit F test was used [15]. *Lepidium sativum* were selected as a test plant. In both tests (Collembolan test and Phytotoxkit F), artificial soil (OECD soil) was used as a reference soil. The bioassays were performed in five replicates.