

PYROLYSIS PRODUCTS AS SOIL FERTILIZERS: SCREENING OF POTENTIALLY HAZARDOUS AROMATIC COMPOUNDS

VLADIMÍR FRIŠTÁK^{1*}, MARION GRASER¹, MARTIN PIPÍŠKA^{2,3},
BARBORA MICHÁLEKOVÁ-RICHVEISOVÁ², GERHARD SOJA¹

¹Energy Department, AIT Austrian Institute of Technology GmbH,
Tulln, 3430, Austria (Vladimir.Fristak@ait.ac.at)

²Department of Ecochemistry and Radioecology, University of SS. Cyril and
Methodius, J. Herdu 2, Trnava, SK-917 01, Slovak Republic

³Department of Chemistry, Trnava University, Trnava, SK-918 43, Slovak Republic

Abstract: This study investigated the concentrations of polycyclic aromatic hydrocarbons (PAHs) in pyrogenic carbonaceous materials (PCM) produced from three waste materials during slow pyrolysis at 400 and 500°C. As feedstocks bone meal (BM), biogas slurry (BC) and chicken manure (CM) were used. As potentially problematic substances 1- and 2- methyl-naphthalene were analysed as indicators for methylated hydrocarbons in pyrolysis products. The phytotoxic effect of soil amendments was evaluated by a standard cress germination test with *Lepidium sativum* L. The analysis showed higher concentrations of the sum of 16 US-EPA PAHs in samples produced at lower temperature and in samples produced from biogas slurry. Concentrations of 1- and 2-methylnaphthalene showed similar trends with concentrations in a range of 35-205% of the sum of 16 PAHs. Germination tests showed inhibition effects of products from biogas slurry when applied in concentrations of ≥ 10 % to standard substrate/. Apparently pyrolysis of biogas slurry requires special attention to avoid accumulation of PAHs and methylated naphthalenes.

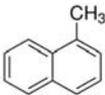
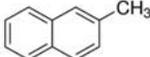
Key words: biochar, PAHs, methylated naphthalene, phytotoxicity

1. Introduction

In a sustainable society renewable resources should substitute non-renewable ones wherever possible. Waste and by-products from various industrial processes and municipal waste are still frequently disposed in landfills whereas in the past they often have been discharged to the sewage water system or to the aquatic environment (FRIŠTÁK and SOJA, 2015). The application of untreated sewage sludges to agricultural land is regionally either completely banned or tightly controlled. Depending on national regulations, mono-incineration of sludge is seen as a promising utilization strategy but the nutrient constituents may be lost if the resulting ash is landfilled. The importance of organic waste and manures recycling to maintain crop production has been recognized by farmers for thousands of years. However, repeated and excess application of these wastes to limited acreage of land has occasionally resulted in excessive nutrient accumulation in soils with subsequent runoff and leaching losses to water bodies, causing water eutrophication and quality deterioration (MORENO-JIMENEZ *et al.*, 2016). Pyrolysis as a carbonization technique that converts organic materials thermo-chemically into recalcitrant aromatic carbon compounds represents a highly effective and reliable treatment method to avoid

nutrient losses and create a more stable material for fertilization (GALAMBOŠ *et al.*, 2015; LEHMANN and JOSEPH, 2015; VÍGLAŠOVÁ *et al.*, 2016). The process requires an inert atmosphere with low or no oxygen and temperatures usually in the range 300-1000°C. For the production of biochar as a nutrient carrier for crops it is necessary to use residual or waste materials (livestock manures, slurries, animal residues, food processing wastes, bones) which need to be monitored for potential contaminations with organic and inorganic xenobiotics. Incomplete combustion and pyrolysis also may cause the formation of polycyclic aromatic hydrocarbons (PAHs). At lower pyrolysis temperature as a main condition for PAH formation dehydrogenation, dealkylation, cyclization and aromatization of present polymers can be observed (HILBER *et al.* 2012). SIMONEIT (1998) mentioned the effect of high pyrolysis temperature on organic compounds from feedstock via cracking into small and highly reactive free radicals followed by pyrosynthesis. In this process free radicals form more stable aromatic structures through recombination reactions. However, the effect of feedstock composition is still not well understood. HALE *et al.* (2012) described this factor as main determinant in the assessment of the aromatic compound formation potential during the carbonization processes. Authors showed the general trends in PAHs formation linked to higher production temperatures. As we know moisture of feedstock and oxygen level as well contribute to PAHs formation during pyrolysis process. Finally pyrolysis time represent important parameter which could enhance the PAHs formation. ZIELENSKA and OLESZCZUK (2015) as well HOSSAIN *et al.* (2011) discussed the effect of pyrolysis temperature and different feedstock composition on the creation of PAHs in sewage sludge-derived biochars. Additionally, pyrolysis products can be also contaminated during pyrolysis by recondensation of pyrolysis vapours (BUSS and MAŠEK, 2014).

Table 1. Comparison of selected physico-chemical properties of naphthalene with 1- and 2-methylnaphthalene.

Property	naphthalene	1-methylnaphthalene	2-methylnaphthalene
Chemical structure			
Molecular weight	128.19	142.20	142.20
Melting point	80.50 °C	-22°C	34.6°C
Boiling point	218°C	244.6°C	241°C
Density at 20°C	1.145 g/mL	1.0202 g/mL	1.0058 g/mL
Solubility in water at 25°C	31.7 mg/L	25.8 mg/L	24.6 mg/L
Soluble in organic agents	alcohol, benzene, ether, acetone	alcohol, ether, benzene	alcohol, ether, benzene
Log K _{OW}	3.29	3.87	3.86
Log K _{OC}	2.97	-	3.39

The application of biochars or pyrolysis products as soil fertilizers with critical concentrations of aromatic compounds can lead to increasing PAHs concentrations fixed on soil structures. Therefore the screening of hazardous aromatic compounds is relevant and much in demand. Generally, in most existing biochar quality standardization protocols the 16 EPA-PAHs of the United States Environmental Protection Agency (USEPA, 2000) have been established as a main quality control parameter to evaluate the potential risk of aromatic compounds in soil amendments for soil contamination. However, recently the scientific discussions have shifted their focus also on methylated structures of naphthalene (Table 1) which could be analyzed in char products from animal residues and bones (WU *et al.*, 2012). These aromatics are present naturally in cigarette smoke, wood smoke, tar, and asphalt. They represent relevant structures which could be included in the assessment of PAHs contamination as an indicator for clean production conditions.

The main aim of this study was to quantify the content of 16 EPA PAHs, 1-methylnaphthalene and 2-methylnaphthalene as new structures in pyrolysis products produced from bone meal, biogas slurry and chicken manure and finally evaluate the potential risk for plant seed germination.

2. Material and methods

2.1 Feedstock preparation and pyrolysis

Commercially available materials such as bone-meal (BM), biogas slurry (BS) and chicken manure (CM) were oven dried or lyophilised (Table 2). Pyrogenic carbonaceous materials (PCM) were produced by slow pyrolysis from all three treated feedstocks at two temperatures (400 and 500°C). Thermochemical conversion was carried out at a residence time of 120 min in a modified lab-scale pyrolysis reactor with nitrogen as flush gas (FRIŠTÁK *et al.*, 2014). After pyrolysis process the resulting products with production yields 30 - 40 % were ground and sieved to achieve a fraction <200 µm. The obtained pyrolyzed samples of bone-meal (BM-PCM), biogas slurry (BS-PCM) and chicken manure (CM-PCM) were directly stored in polypropylene boxes under dry and cool (4 °C) conditions for further characterization and experiments.

Table 2. Feedstock characterization, pre-treatment and conditions of pyrolysis process.

Sample	Feedstock	Pre-treatment	Pyrolysis conditions
BM 400	Bone-meal	Drying 60°C/72 h	400°C / 2h / N ₂
BM 500	Bone-meal	Drying 60°C/72 h	500°C / 2h / N ₂
BS 400	Biogas slurry	Lyophilisation	400°C / 2h / N ₂
BS 500	Biogas slurry	Lyophilisation	500°C / 2h / N ₂
CM 400	Chicken manure	Lyophilisation	400°C / 2h / N ₂
CM 500	Chicken manure	Lyophilisation	500°C / 2h / N ₂

2.2 Pyrolysis products characterization

The active pH values of samples were measured after mixing the samples with deionized water (ratio 1:15 m/v) for 1 h and 1 h of stabilization. Electrical conductivities (EC) of samples were measured in deionized water (1:10 m/v) after 24h of mixing. The total contents of C, H, N and S in samples were determined using a CHNS-O Elemental Analyzer (CHNS-O EA 1108, Carlo Erba Instruments, Italy). Total Cd, Cu and Pb concentrations in materials were determined using ICP-MS (Perkin Elmer, Elan DRCe 9000, USA) after wet digestion with HNO₃ and H₂O₂ (ENDERS and LEHMANN, 2012).

2.3 Determination of PAHs in pyrolysis products

The total concentrations of the 16 US-EPA PAHs in pyrogenic carbonaceous materials were determined by Soxhlet extraction (toluene, solid/liquid: 1/15, 6h, 120°C) and a modified method described by HILBER et al. (2012). For comparison ethyl-acetate (solid/liquid: 1/15, 6h, 80°C) as extraction agent was used as alternative extractant. The obtained toluene and ethyl-acetate extracts were evaporated to 1 ml using a rotary vacuum concentrator. After purification and filtration, the concentrated extracts were analysed by HPLC coupled with DAD ($\lambda = 310$ nm) and FLD (Ex = 260 nm, Em = 350 nm, 420 nm, 440 nm, 500 nm) detectors. 16 US-EPA PAHs standard solution (MERCK, Germany) was used to prepare internal standard solutions of known concentrations.

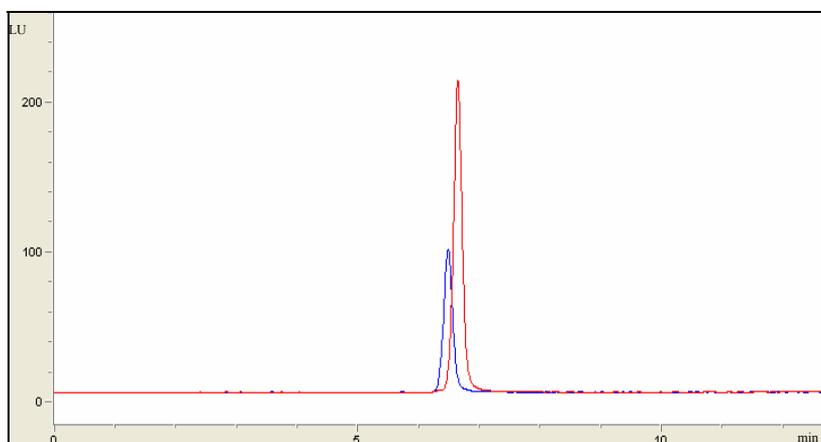


Fig. 1. Characteristic chromatogram of a standard with 2 mg L⁻¹ 1-methylnaphthalene (—) and 4 mg L⁻¹ 2-methylnaphthalene (—).

The chromatographic apparatus consisted of a Agilent 1100er series model, degasser G1379A, quaternary pump G1311A, column GRACE/Vydac® C18 polymeric reversed-phase, 4.6 × 250 mm, 5 μm and GRACE/ Vydac® C18 guard

column, 4.6×7.5 mm, $5\mu\text{m}$. The composition of mobile phase as a mixture of ultra-pure water and acetonitrile varied during time of analysis. The determination of 1- and 2-methylnaphthalene was done in the extracts of BMPCM, BSPCM and CMPCM with the analogue design of HPLC coupled to FLD detector ($E_x = 260$ nm, $E_m = 350$ nm). Standard solutions of 1- and 2-methylnaphthalene (250 mg L^{-1} , MERCK, Germany) were used to prepare internal mix solutions at known concentrations. The limit of detection (LOD) and limit of quantification (LOQ) for both substances were determined as $8 \mu\text{g L}^{-1}$ and $20 \mu\text{g L}^{-1}$, respectively. Good repeatability (RSD 0.4 % (1-methylnaphthalene) and 1.3 % (2-methylnaphthalene) and linearity of the applied method was confirmed for the range $0.05\text{--}125 \text{ mg L}^{-1}$. Characteristic chromatograms of studied substances are shown in Fig. 1.

2.4 Germination test

The potentially phytotoxic effects of pyrolysis products were assessed with a germination test according to a standardized method (ÖNORM S2023). Briefly, test materials BM-PCM 400, BM-PCM 500, BS-PCM 400, BS-PCM 500 CM-PCM 400 and CM-PCM 500 were mixed with the standard substrate (mixture of Einheitserde ED63 (natural clays, peat, block peat) and sand; 9:1) in proportions of 10 and 30% and moistened to 60 % water holding capacity. The substrate samples were placed in pots according to the experimental design shown in Fig. 2, followed by incorporation of 30 cress seeds (*Lepidium sativum* L.). The germination rate was determined during the first 6 days of growth under greenhouse conditions (22°C , light period l/d 12/12h) and constant water content.

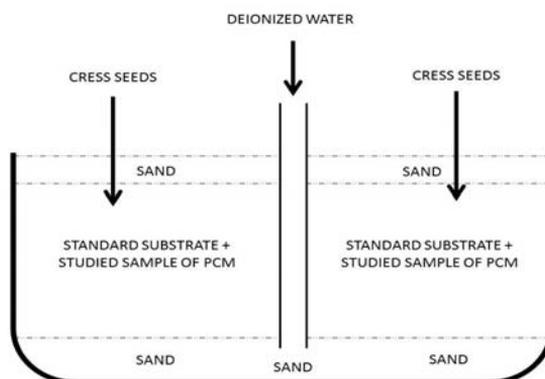


Fig. 2. Experimental design of pot layout for cress-germination test.

3. Results and discussion

3.1 Elemental characteristics of pyrolysis products

Basic physico-chemical characterizations of pyrogenic carbonaceous materials BM-PCM 400, BM-PCM 500, BS-PCM 400, BS-PCM 500 CM-PCM 400 and CM-

PCM 500 showed slight differences in pH and EC between samples prepared at 400 and 500°C. Generally pH increased in the order of BM-PCM (9.9-10.0) < CM-PCM (10.1-10.2) < BS-PCM (10.4-10.5).

Table 3. Elemental analyses of studied pyrolysis products; for sample abbreviations see Table 2.

Sample	C* (%)	H* (%)	N* (%)	S* (%)	Cd mg kg ⁻¹	Cu mg kg ⁻¹	Pb mg kg ⁻¹
BM-PCM 400	30.3	2.5	5.2	2.3	<0.01	19.04 ± 0.51	<1
BMPCM 500	33.9	1.3	5.0	1.8	0.11 ± 0.01	21.10 ± 1.24	<1
BSPCM 400	35.3	2.6	2.1	12.0	0.37 ± 0.02	80.08 ± 0.47	8.44 ± 0.47
BSPCM 500	29.7	1.9	1.8	9.6	0.43 ± 0.02	81.47 ± 0.21	10.07 ± 0.45
CMPCM 400	44.8	2.6	4.4	8.7	0.63 ± 0.02	98.54 ± 1.27	2.77 ± 0.02
CMPCM 500	46.3	1.6	4.1	8.4	0.64 ± 0.01	110.01 ± 1.98	3.09 ± 0.01

* values represent means of 5 material measurements with SD lower than 1%

Determination EC values showed values 4.75 ± 0.25 mS cm⁻¹ for BM-PCM, 4.08 ± 0.12 mS cm⁻¹ for CM-PCM and 10.36 ± 0.58 mS cm⁻¹ for BS-PCM. The trends in pH and EC values of pyrolysis products reflect similar trends in feedstocks characteristics (data not shown). Elemental analyses (Table 3) confirmed differences in C, H, N and S contents of materials prepared from different bio-waste feedstocks. As the pyrolysis temperature increased, the total carbon concentrations of bone meal and chicken manure-derived pyrogenic carbonaceous material increased, while hydrogen, nitrogen and sulphur decreased. At higher pyrolysis temperatures some amorphous carbon could have been converted into aromatic carbon (KEILUWEIT *et al.*, 2010; REN *et al.*, 2016). Additionally, with rising temperature an increased volatilization of proteins and decomposition of remaining lignocelluloses can be observed (TSAI *et al.*, 2012). REN *et al.* (2016) showed after pyrolysis of pig manure increases in total C content, dependent on pyrolysis temperature. Their pig manure-derived materials pyrolyzed at 300°C contained more than 62 % total C. As we realized the chicken manure feedstock contained a variable amount of straw which could affect total carbon content in pyrolysis products. In our study PCM-products produced by thermochemical conversion of biogas slurry showed slightly increasing total C, H, N and S contents at lower temperature. These heterogeneous mixtures which are characterized by comparable compositions to sewage sludges apparently contain more volatile compounds and have potentially lower lignocellulosic content. By pyrolysis of these materials a carbon content of 28-35 % can be reached in the pyrogenic products, depending on temperature. Additionally, Table 3 shows the total Cd, Cu and Pb concentrations which were 1.5 - 2 folds higher compared to metal contents in feedstocks due to H, N and O losses. Organic wastes such as biosolids, slurries and

sludges are generally known to contain high concentrations of potentially toxic elements (PTEs) which remain in the final pyrogenic products (LU *et al.*, 2013). CELY *et al.* (2015) showed similar contents for comparison of different manure-based pyrolysis products and evaluation of their agronomic properties. Our results revealed relatively high sulphur and lead contents in BS-PCM samples which can be one of the factors to restrict the application of these heterogeneous materials as soil amendments. Elevated concentrations of PTEs in soil fertilizers can affect seed germination and plant metabolism. Most of the PTEs concentrations in studied materials were lower as thresholds permitted by European Biochar Certificate EBC (2012) such as Cd <1.5 mg kg⁻¹, Cu <100 mg kg⁻¹ and Pb <150 mg kg⁻¹. SINGLA *et al.* (2014) found in digested slurry-derived pyrolytic materials produced at 330-370°C concentrations of 0.4 mg Cd kg⁻¹, 76 mg Cu kg⁻¹ and 2.5 mg Pb kg⁻¹.

3.2 PAH concentrations

Polycyclic aromatic hydrocarbons are produced during pyrolysis process of lignocellulose materials and are dependent on pyrolysis temperature (LEHMANN and JOSEPH, 2015). High temperatures (>600°C) during pyrolysis of plant residues were reported to be propitious for reducing the content of PAHs due to nuclear condensation into large, non-extractable sheets and strong sorptive retention by condensed phases (QIU *et al.*, 2016). However, in case of more heterogeneous feedstocks such as slurries, sludges and manures this trend can be completely different. Our analyses revealed quite variable concentrations of the sum of 16 PAHs in bone meal- (BM-PCM), biogas slurry- (BS-PCM) and chicken manure- (CM-PCM) derived pyrogenic carbonaceous materials produced at 400 and 500°C (Table 4). We could not confirm the direct dependence of 16 US-EPA PAHs concentrations on the temperature of thermochemical conversion.

Table 4. Mean concentrations of Σ 16 EPA PAH compounds, 1- and 2- methyl-naphthalene in toluene extracts of bone meal- (BM-PCM), biogas slurry- (BS-PCM) and chicken manure- (CM-PCM) derived pyrogenic carbonaceous materials produced at 400 and 500°C.

Sample	Σ 16 EPA PAHs	1-methylnaphthalene	2-methylnaphthalene
BMPCM 400	4.87 ± 0.47	0.69 ± 0.03	2.51 ± 0.04
BMPCM 500	5.56 ± 0.58	1.16 ± 0.08	2.83 ± 0.08
BSPCM 400	37.97 ± 2.13	8.76 ± 0.45	20.35 ± 0.84
BSPCM 500	24.20 ± 2.45	2.96 ± 0.98	5.43 ± 1.85
CMPCM 400	6.18 ± 0.41	1.86 ± 0.08	7.34 ± 0.55
CMPCM 500	3.35 ± 0.12	1.81 ± 0.11	5.08 ± 0.13

Samples produced from bone meal and chicken manure showed generally lower levels than the limits established in the European Biochar Certificate for basic quality but not for premium quality (EBC, 2012). On the other hand, samples BS-PCM 400 and BS-PCM 500 exceeded the basic quality thresholds for the sum of 16 US-EPA PAHs, with the highest concentrations for phenanthrene, fluorene, naphthalene and chrysene. Naphthalene was the major contributor (>65%) to the total PAHs content in

samples derived from biogas slurry. The extraction efficiency tested by toluene and ethyl-acetate extraction protocols showed similar and comparable results (R^2 0.87).

3.3 Concentrations of 1-methylnaphthalene and 2-methylnaphthalene

Methylated PAHs such as 1- and 2- methylnaphthalene provide 10-20 times lower degradation efficiency and thus are more persistent in water and aquatic ecosystems compared to non-methylated naphthalene (HEITKAMP and CERNIGLIA, 1987). Determination of concentrations of both chemical compounds (Fig. 4) in toluene and ethyl-acetate extracts of studied samples showed similar trend as in Σ 16 US-EPA PAHs contents. Generally, contents of 1-methylnaphthalene and 2-methylnaphthalene increased in order BM-PCM < CM-PCM < BS-PCM.

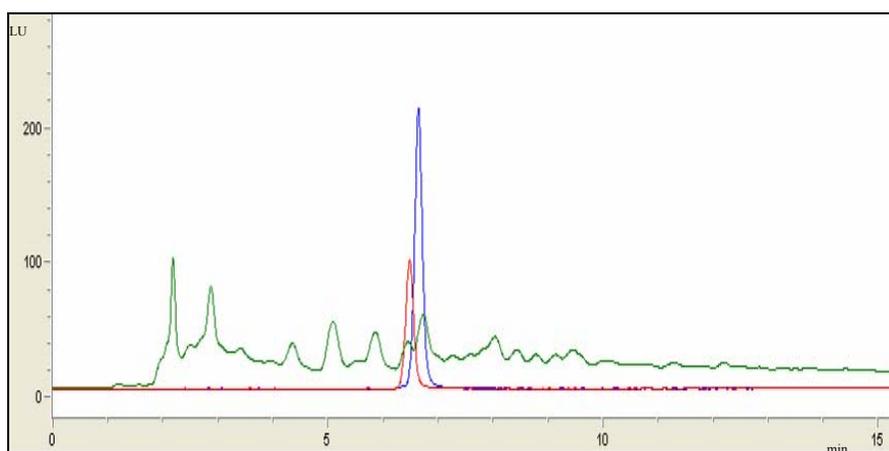


Fig. 4. Characteristic chromatograms of standard 1-methylnaphthalene (—) at concentration 2 mg L^{-1} , 2-methylnaphthalene (—) at concentration 4 mg L^{-1} and ethyl acetate extract of BS-PCM produced 500°C (—).

The highest concentrations were determined in samples produced from biogas slurry and chicken manure at 400°C . Concentrations of methylated structures represented 35-205 % of the sum of 16 US-EPA PAHs in the analysed samples. This fact showed a potential risk to be considered in the assessment of carbonaceous materials as soil fertilizers. For comparison, SHACKLEY *et al.* (2012) found concentrations of 1.77 and 1.36 mg kg^{-1} for 1-methylnaphthalene and 2-methylnaphthalene, respectively, in rice husk char produced by gasification process. However, standardized concentration thresholds for these chemical structures in potential soil fertilizers produced from heterogeneous materials such as sludges or slurries are still missing and provide a new question in environmental policy for this kind of products.

3.4 Germination test of pyrolysis products

Germination rates of cress seeds (*Lepidium sativum* L) were affected by all tested materials when 10 or 30% were added to the growth substrate (Fig. 5). The higher

application rate of pyrolysis materials intensified adverse effects or reduced positive effects on cress germination. In comparison with control (non-amended sample) CM-PCM400 and CM-PCM500 samples in 10% application rate showed positive effects and BS-PCM400, BS-PCM500 negative effect on seeds germination. At samples BM-PCM400, BM-PCM500 no significant change was observed compared to control. 30% application rate showed 10-20% reduction compared to an addition rate of 10%. Positive or neutral effects on cress germination were confirmed at CM-PCM500 and CM-PCM400 treatments. On the other hand, BS-PCM400, BS-PCM500, BM-PCM400, and BM-PCM500 showed significantly negative effects on germination rates. This trend is in accordance with the chemical characterizations of PAH concentrations and metals (such as Cd and Cu) that apparently pose a risk by releasing germination inhibitors when PCMs are applied in such high concentrations as in these tests.

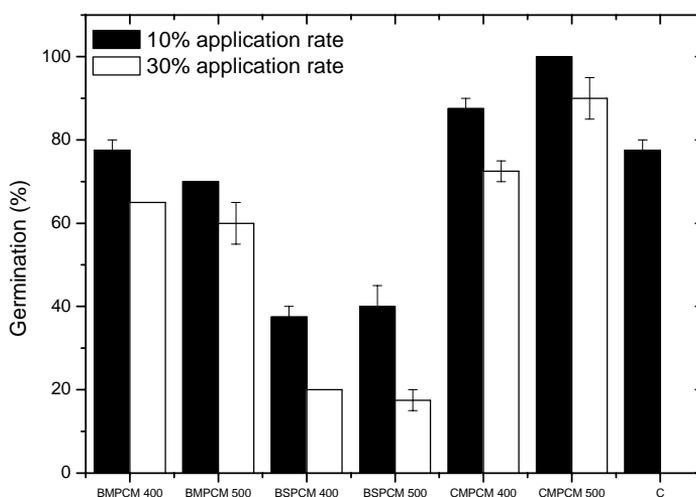


Fig. 5. Effects of 10 and 30% application rates of bone meal-, biogas slurry- and chicken manure-derived pyrogenic carbonaceous materials on germination rate (%) of cress seeds after 6 days. Values represent means \pm SD (n=3).

A phytotoxic influence of mobile organic compounds on cress germination was extensively described by BUSS and MAŠEK (2014). The authors identified specific volatile organic compounds (vapours) and pyrolysis liquids (mainly crude-oils) which could play a role in inhibition of biochemical and biological processes. As mentioned before, pyrolysis products could be contaminated by production and re-condensation of various organic compounds during the pyrolysis process. Subsequently, a solid pyrolysis product can release organic structures which may become toxic for biological systems and can have an adverse effect on germination. Based on these scenarios, it is required to take a closer look on product characteristics not only of the solid but also of the liquid and gaseous fraction. More volatile forms such as phenolic substances could be relevant for phytotoxic effect evaluation (LENTZ and IPPOLITO,

2012). Due to their micro-structure and high porosity, biochars and pyrogenic carbonaceous products provide a large storage potential for such substances. The study of new structures (PAHs, phenolic species) which could be relevant during the carbonization process should be incorporated into the quality control of new pyrolysis products which are intended as soil amendments.

4. Conclusions

Re-condensation of liquid and gaseous substances during the pyrolysis process resulted in pyrogenic carbonaceous materials with partially high content of organic compounds that could have phytotoxic effect. The quantification of standardized sum of 16-USEPA PAHs and methylated naphthalene structures showed a potential risk in utilization of heterogeneous waste materials such as biogas slurry for fertilizer production. Our study confirmed for concentrations of PAHs the possibility to comply with EBC thresholds (4 or 12 mg kg⁻¹ resp.) for materials produced from chicken manure and bone meal. These materials showed no-toxic effects in germination tests with cress seeds. When using biogas slurry as feedstock, PAH accumulation in the pyrolysis product has to be carefully observed and effectively avoided by advanced management of volatiles in the reactor.

Acknowledgment: The authors thank the Austrian FFG for financial support of the Research Studio FERTI-MINE, project nr. 844744.

References

- BUSS, W., MAŠEK, O.: Mobile organic compounds in biochar – A potential source of contamination – Phytotoxic effects on cress seed (*Lepidium sativum*) germination. *J. Environ. Manage.*, 137, 2014, 111-119.
- CELY, P., GASCÓ, G., PAZ-FERREIRO, J., MÉNDEZ, A.: Agronomic properties of biochars from different manure wastes. *J. Anal. Appl. Pyrolysis.*, 111, 2015, 173-182.
- ENDERS, A., LEHMANN, J.: Comparison of wet-digestion and dry-ashing methods for total elemental analysis of biochar. *Commun. Soil Sci. Plan.*, 43, 2012, 1042-1052.
- FRIŠTÁK, V., SOJA, G.: Effect of wood-based biochar and sewage sludge amendments for soil phosphorus availability. *Nova Biotechnol. Chim.*, 14, 2015, 104-104.
- GALAMBOŠ, M., DAŇO, M., VÍGLAŠOVÁ, E., KRIVOSUDSKÝ, L., ROSSKOPFOVÁ, O., NOVÁK, I., BEREK, D., RAJEC, P.: Effect of competing anions on perchlorate adsorption by activated carbon. *J. Radioanal. Nucl. Chem.*, 304, 2015, 1219-1224.
- HALE, S.E., LEHMANN, J., RUTHERFORD, D., ZIMMERMANN, A.R., BACHMANN, R.T., SHITUMBANUMA, V., O'TOOLE, A., SUNDQVIST, K.L., ARP, H.P.H., CORNELISSEN, G.: Quantifying the total and bioavailable polycyclic aromatic hydrocarbons and dioxins in biochars. *Environ. Sci. Technol.*, 46, 2012, 2830-2838.

- HEITKAMP, M.A., CERNIGLIA, C.E.: effects of chemical structure and exposure on the microbial degradation of polycyclic aromatic hydrocarbons in fresh water and estuarine ecosystems. *Environ. Toxicol. Chem.*, 6, 1987, 535- 546.
- HILBER, I., BLUM, F., LEIFELD, J., SCHMIDT, H.P., Bucheli, T.D.: Quantitative determination of PAHs in biochar: a prerequisite to ensure its quality and safe application. *J. Agric. Food Chem.*, 60, 2012, 3042-3050.
- HOSSAIN, M.K., STREZOV, V., YIN CHAN, K., NELSON P.F.: Agronomic properties of wastewater sludge biochar and bioavailability of metals in production of cherry tomato (*Lycopersicon esculentum*). *Chemosphere*, 78, 2010, 1167-1171.
- KEILUWEIT, M., NICO, P.S., JOHNSON, M.G., KLEBER, M.: Dynamic molecular structure of plant biomass-derived black carbon (biochar). *Environ. Sci. Technol.* 44, 2010, 1247-1253.
- LEHMANN, J., JOSEPH, S.: Biochar for environmental management: Science, Technology and Implementation. Earthscan from Routledge: London, UK, 2015, 944pp.
- LENTZ, R.D., IPPOLITO, J.A.: Biochar and manure affect calcareous soil and corn silage nutrient concentrations and uptake. *J. Environ. Qual.*, 41, 2012, 1033-1043.
- LU, H., ZHANG, W., WANG, S., ZHUANG, L., YANG, Y., QIU, R.: Characterization of sewage sludge-derived biochars from different feedstocks and pyrolysis temperatures. *J. Anal. Appl. Pyrol.*, 102, 2013, 137-143.
- MORENO-JIMENEZ, E., FERNÁNDEZ, J.M., PUSCHENREITER, M., WILLIAMS, P. N., PLAZA, C.: Availability and transfer to grain of As, Cd, Cu, Ni and Zn in a barley agri-system: Impact of biochar, organic and mineral fertilizers. *Agric. Ecosyst. Environ.*, 219, 2016, 171-178.
- ÖNORM S 2023: Untersuchungsmethoden und Güteüberwachung von Komposten. Front Cover. Österreichisches Normungsinstitut, 1993 - 16 pages.
- QIU, M., SUN, K., JIN, J., HAN, L., SUN, H., ZHAO, Y., XIA, X., WU, F., XING, B.: Metal/metalloid elements and polycyclic aromatic hydrocarbon in various biochars: The effect of feedstock, temperature, minerals, and properties. *Environ. Pollut.*, 206, 2015, 298-305.
- REN, X., SUN, H., WANG, F., CAO, F.: The changes in biochar properties and sorption capacities after being cultured with wheat for 3 months. *Chemosphere*, 144, 2016, 2257-2263.
- SHACKLEY, S., CARTER, S., KNOWLES, T., MIDDELINK, E., HAEFELE, S., SOHI, S., CROSS, A., HASZELINE, S.: Sustainable gasification-biochar systems? A case-study of rice-husk gasification in Cambodia, Part I: Context, chemical properties, environmental and health and safety issues. *Energy Pol.*, 41, 2012, 618-623.
- SIMONEIT, B.R.: Biomarker PAHs in the environment. In NEILSON, A.H. (Ed.) PAHs and related compounds. Springer, Berlin, 1998, pp. 175-221.
- SINGLA, A., DUBEY, S.K., SINGH, A., INUBUSHI, K.: Effect of biogas digested slurry-based biochar on methane flux and methanogenic archaeal diversity in paddy soil. *Agric. Ecosyst. Environ.* 197, 2014, 278-287.
- US-EPA: Process design manual, land application of sewage sludge and domestic septage. Office of Research and Development, Washington, DC, United States Environmental Protection Agency, EPA/625/R-95/001, 1995.

- VÍGLAŠOVÁ, E., DAŇO, M., GALAMBOŠ, M., ROSSKOPFOVÁ, O., RAJEC, P., NOVÁK, I.: Column studies for the separation of ^{99m}Tc using activated carbon. *J. Radioanal. Nucl. Chem.*, 307, 2016, 591-597.
- WU, X., MARKHAM, J., SUN, X., WANG, D.: Optimizing catalytic fast pyrolysis of biomass for hydrocarbon yield. *Transactions of ASABE*, 55, 2012, 1879-1885.
- ZIELIŃSKA, A., OLESZCZUK, P.: The conversion of sewage sludge into biochar reduces polycyclic aromatic hydrocarbon content and ecotoxicity but increases trace metal content. *Biomass Bioenerg.*, 75, 2015, 235-244.

Received 23 March 2016

Accepted 6 July 2016