Evaluation of the lipid fraction of pyrochars organic matter in the aspect of negative effects on soil

Rodion Okunev*, *Elena* Smirnova, *Kamil* Giniyatullin, and *Irina* Guseva

Institute of Environmental Sciences, Kazan Federal University, 420008 Kazan, Russia

Abstract. The evaluation of the possible negative effect of pyrochars on soils based on the analysis of the content of lipid fraction and polycyclic aromatic hydrocarbons (PAHs) of organic matter was evaluated. Eight species of pyrochar were obtained from the crop and wood residues (linden, willow, corn, millet) by two pyrolysis regimes: low-temperature pyrolysis (<400°C) and high-temperature pyrolysis (400–600°C). The largest amount of lipid fraction (from 0.54 to 2.78%) and PAHs were found in pyrochars obtained at a low pyrolysis temperature. The total content of PAHs in the studied samples ranged from 8.49 to 603.21 μg/kg. According to the PAHs content, pyrochar was the most adverse for application to the soil, obtained from the residues of millet of low-temperature pyrolysis, however, at a high pyrolysis temperature, the safest product with the lowest PAHs concentration and a significant amount of lipid fraction was formed. Using an incubation experiment by measuring substrate-induced respiration in soil-pyrochar mixtures, it was shown that the application of this meliorant can also increase the emission of carbon dioxide from soils in a short time. The results of the experiments showed that it is necessary to precisely control the conditions of pyrolysis and carefully select the material for pyrochar in order to obtain the products with most favourable amounts of lipid fraction and PAHs content.

1 Introduction

Pyrochar is a meliorant obtained by pyrolysis of organic material. Their application to soils can be considered as a way to climate change mitigation and changing the properties of soils in order to increase their fertility. In addition, pyrochars are used for other purposes: as sorbents for heavy metals, pesticides, various ions, organic pollutants, and to protect nutrients from the leaching [1, 2]. From the agrochemical point of view, pyrochar is a carbon source that is more resistant to microbiological degradation [3].

Pirochars are made from various plant materials (crop residues, wood residues, livestock product residues) under different time-temperature conditions of pyrolysis. Regardless of the pyrolysis conditions, the final product contains (or may contain) a certain amount of labile organic matter, which may include organic pollutants. During the pirochar obtaining process, significant amounts of acetic acid, methanol, and phenolic compounds are released [4].

In the obtained products, along with benzene polycarboxylic acids, which are inert components of the product, a significant part of the carbon is represented by humic substances, glycolipids, phospholipids, and others [2], when pyrochars are introduced into the soils, can partially replenish the fraction of soil lipids. The introduction of pyrochars with a high lipid content into the soil can have a positive effect by providing soil biota with available organic matter [2, 5]

However, pyrochars with a high lipid fraction can theoretically have a negative effect due to the deterioration of soil properties or entrance with them hazardous pyrolysis products such as polycyclic aromatic hydrocarbons (PAHs). A significant proportion of PAHs is inevitably formed during the production of pyrochar, which poses a threat due to their stability in the environment and an increase of intensity of pyrochar application in agriculture [6].

The main precursors of PAHs that formed during pyrolysis are cellulose, hemicellulose, and lignin [7], the contents of which varies greatly in plants of different species, which provides strong differences in the concentrations of PAHs in pyrochars of various origin [6].

The second factor, which strongly affects both the qualitative and quantitative composition of PAHs, and the lipid component of product, is the pyrolysis process [8]. The main danger to humans is the carcinogenic, immunotoxic, teratogenic properties of PAHs. After entering through the food chain to the human body, they interfere with the function of cell membranes and enzyme systems [9].

Another possible negative effect is associated with the influence of an additional source of organic matter introduced with pyrochars into the soil on the activity of microorganisms. High lipids and other organic substances content as an additional food source can have stimulating effect on the soil microbes, and leading to increase in CO_2 emissions from the soil. However,

* Corresponding author: tutinkaz@yandex.ru

pyrochar application was originally promoted as an effective solution for carbon sequestration and reducing greenhouse gas emissions from soils. Further studies have shown the presence of a short-term increase in carbon dioxide emissions after their application [10]. However, according to other researchers, pyrochar does not have a significant effect on CO_2 fluxes in the soil [11]. Despite the presence of a large number of studies of their effect on soil respiration, the question of the influence of pyrochars labile organic matter on this indicator remains open.

The purpose of this research was to evaluate the possible negative effect of the organic components of pyrochars on the soils. For this, the content of the lipid fraction and the concentration of PAHs in pyrochars of various origins were studied. To study the effect of pyrochars organic matter on soil microorganisms, an incubation experiment with the introduction of pyrochar into soils and the measurement of substrate-induced soil respiration (SIR) was carried out.

2 Materials and methods

For the experiments, pyrochar samples (8 species) prepared from various wood and grass materials in different modes of slow pyrolysis under two thermal conditions were used. Pre-cut samples were initially crushed to the size of the chips with a knife crusher. Then, 50 g samples were pyrolyzed in a laboratory retort d = 32 mm in a muffle furnace under various temperature conditions with discharging a steam-gas mixture through a condenser. Pyrochar samples of the crop residues of millet and maize, willow and linden sawdust were obtained at temperatures <400°C (low-temperature pyrochars) and 400–600°C (high-temperature pyrochars) with slow pyrolysis (10°C/min) for 170 min. Figures and tables, as originals of good quality and well contrasted, are to be in their final form, ready for reproduction, pasted in the appropriate place in the text.

The general chemical properties of pyrochars are presented in Table 1.

Table 1. Chemical properties of pyrochars.

Plants used for pyrolysis	Pyrolysis temperature	Total C, N and ash content, %		
		C	N	Ash
Linden	400–600°C	–	–	–
Willow		79.6	0.28	6.8
Corn		66.3	0.86	19.9
Millet		71.2	0.66	13.9
Willow	< 400°C	77.3	0.23	2.7
Corn		63.1	0.47	8.3
Millet		71.9	0.16	3.6
Linden		–	–	–

The free lipid fraction was extracted with a mixture of ethyl alcohol:benzene (1:1) in Soxhlet extractor for 48 hours. The extract was adjusted to a volume of 250 ml. The total lipid content was determined gravimetrically after evaporation of the alcohol-benzene mixture from an aliquot of the extract. The obtained free lipid residue was dried at 50°C for 48 hours before weighing. The content of organic carbon (Corg) was determined by wet burning according to the method of Tyurin [12]. PAHs were isolated from pyrochars with a mixture of acetone:cyclohexane (1:1) in Soxhlet extractor and were determined on Flexar HPLC (Perkin Elmer, USA) according to the procedure described in [13].

The study of the pyrochar samples morphology has been performed with field emission scanning electron microscope (SEM) Merlin (Carl Zeiss). Surface morphology was surveyed with an accelerating voltage of primary electrons of 5 kV and probe current of 300 pA for the minimal impact on the object of investigation.

For incubation experiment the samples of the humus horizon of gray forest soil obtained from a depth of 5–20 cm were used. The fresh soil was passed through a 2 mm, 40 g of the sample was mixed with 2 g of pyrochar passed through a 1 mm sieve. Mix was placed in Petri dishes, adjusted to a moisture content of 55% of maximum field capacity and thoroughly stirred. Petri dishes with model mixtures are stored in a thermostat with periodic ventilate to provide free access of oxygen. The SIR was determined after 3 months and 6 months of incubation.To determine the SIR, from the model mixture by small portions from different parts of the Petri dish an average sample (2.5 g) was placed in a vials (20 ml) with hermetically sealed rubber stopper. The estimated amount of the glucose solution (10 mg per 1 g of the mix) was added by the laboratory dispenser, so that the final moisture content of the material corresponded to 65% of the maximum field capacity. The vials were stored in a thermostat for 4 hours at t = 25 °C, the gas phase was sampled using a syringe. The determination of CO_2 was performed on a Clarus 580 gas chromatograph (PerkinElmer) with a thermal conductivity detector. The intensity of the SIR was expressed in μg C-CO_2, released by 1 g of the model mixture for 1 hour. For statistical evaluation of the results, ANOVA was used. The calculations were performed in the program STATISTICA 8.0.

3 Results and discussion

Table 2 presents the studied characteristics of pyrochars. The total PAHs content in the samples varied in the range from 8.49 to 603.21 μg/kg. A similar range of values was found for corn, oak and pine wood in the study [14], for remains of millet and other tree species – in [15]. The average content of PAHs in pyrochars obtained at a pyrolysis temperature of < 400°C is 198.0±301.8 μg kg^{-1} while in pyrochars obtained at a high temperature it is much lower – 26.6±5.6 μg kg^{-1} (Fig.1b). The lowest pollutant content was found for pyrochar from maize, residues of millet and willow wood during high-temperature pyrolysis. It is possible that amorphous phases volatilize at a high temperature (≥500°C), which minimizes the concentration of extractable PAHs on the surface of pyrochars [16]. The highest concentration of pollutants is typical for corn and millet pyrochars obtained in low temperature pyrolysis.

The largest amount of lipid fraction (from 0.54 to 2.78% by weight of pyrochar) was found in pyrochars obtained at a low pyrolysis temperature (Table 2, Fig. 1a). Its maximum content was found in products from the remains of corn and millet. Pyrochars obtained in the temperature range 400–600°C are characterized by a low content of lipid fraction – from 0.1 to 0.46% by weight. The smallest content is observed in products from tree species, the largest – from herbaceous plants.

Table 2. Content of the lipid fraction and PAHs in pyrochars

Pyrochar type	Pyrolysis tempe-rature	Content of lipid fraction, %	Content of C_{org} in lipid fraction,%	PAHs content, μg kg^{-1}
Linden	400–600°C	–	–	71.16
Willow		0.16	0.13	8.61
Corn		0.46	0.31	18.32
Millet		0.38	0.19	8.49
Willow	< 400°C	0.54	0.26	53.95
Corn		3.38	2.1	111.58
Millet		2.78	1.84	603.21
Linden		–	–	23.37

The lipid fraction getting into the soil with pyrochars is a source of organic carbon for microorganisms. However, the composition of this fraction may contain most of the PAHs that we identified, which will adversely affect to soil microorganisms. Therefore, in order to identify the most comfortable conditions for the life of microorganisms, the ratios between the content of the lipid fraction and PAHs concentrations in pyrochar were calculated.

The highest value of the ratio was found for the product obtained from millet residues of high temperature pyrolysis ($4.5 \bullet 10^5$) (Table 3). Then this pyrochar can be considered like the safest and most favourable for application as a meliorant, and despite the high PAHs content – corn pyrochar (low temperature pyrolysis), since these samples contain the largest amount of organic matter in the form of a lipid fraction.

Table 3. Some properties of obtained pyrochars

Pyrochar type	Pyrolysis temperature	The amount of PAHs introduced to soil with pyrochar at dose of 5%	Ratio of lipid fraction content to the PAHs concentration ($n10^5$)
Linden	400–600°C	3.56	–
Willow		0.43	1.9
Corn		0.92	2.5
Millet		0.42	4.5
Willow	< 400°C	2.7	1.0
Corn		5.58	3.0
Millet		30.16	0.5
Linden		1.17	–

Using samples of products obtained from the remains of corn and willow wood, we compared the surface images of pyrochars obtained using emission scanning electron microscope. Figure 2 shows the SEM images of microstructure of corn pyrochars obtained in high (a) and low (b) pyrolysis temperature. The images show pores and cells that repeat the vessels and nutritional channels of plants. Most pores are between 10 and 50 microns in size. These pores are most suitable for the growth and development of microorganisms, accumulation and protection of nutrients from leaching.

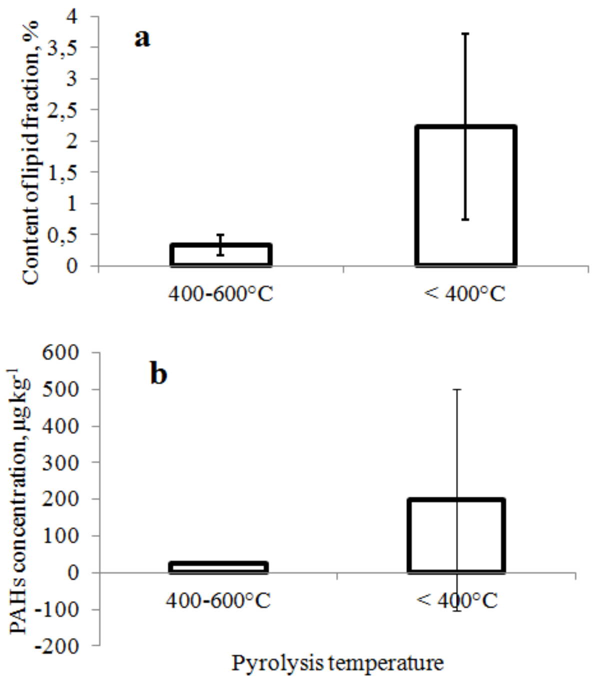

Fig. 1. Average content of the lipid fraction and PAHs in pyrochars obtained at low and high pyrolysis temperatures.

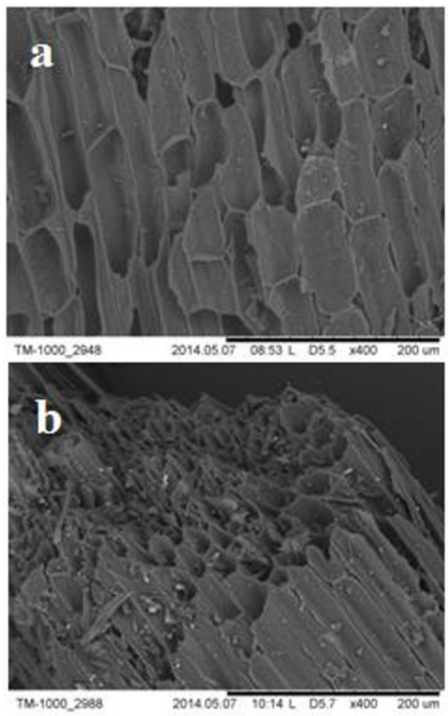

Fig. 2. SEM images of high (a) and low (b) pyrolysis corn pyrochar

The main difference between the pyrochar images of low-temperature pyrolysis corn and the product obtained by high-temperature pyrolysis is the presence on the surface of a large number of small formations, which can presumably be accumulations of mineral and organic substances – the remains of plant structures that under high-temperature conditions are completely pyrolyzed.

On images of low-temperature pyrolysis pyrochars from willow wood the accumulations of small structures are also shown, however, these formations are less in comparison with corn pyrochar (Fig. 3).

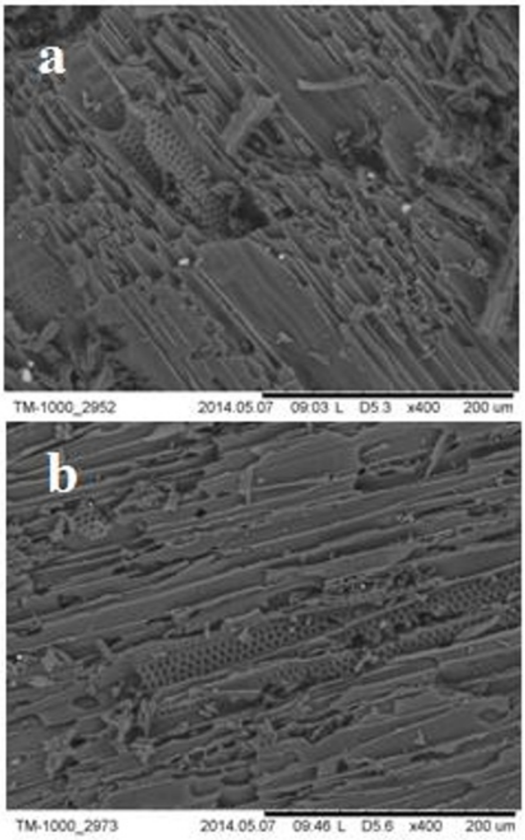

Fig. 3. SEM images of high (a) and low (b) pyrolysis willow pyrochar.

These organic or organic-mineral fractions can effect to soil microorganisms activity. Figure 4 shows the SIR intensity in model mixes with native pyrochars obtained at different temperatures on the 30th and 60th days of the experiment. From the diagram it can be seen that the addition of pyrochars to the soil led to a significant increase of the intensity of the SIR on the 30th day of incubation. The labile easily available carbon that entered with pyrochars in the short-time period had a positive effect on the activity of microorganisms, as shown in the works [17].

However, after 60 days of incubation, a difference in CO_2 emissions between the control soil and soil-pyrochar mixes is not detected. A longer incubation, although it leads to the establishment of equilibrium in the soil-pyrochar system, which ensures homogeneity of the mixture and reliable determination of the SIR value, it also reduces the reliability of the evaluation of respiratory activity due to a general decrease in respiration rate. This decrease is probably due to the reduction in the content of labile fractions introduced together with pyrochar, which are eventually used by microorganisms. In the 30-day period, the highest emission was found in a mixture with low-temperature pyrolysis linden pyrochar (250°C). This is explained by the fact that at low pyrolysis temperatures more labile organic matter fractions are formed, which actively interact with soil microorganisms.

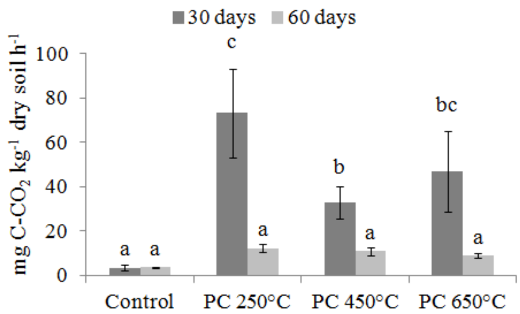

Fig. 4. SIR in model mixes with linden pyrochars obtained at different pyrolysis temperatures on the 30th and 60th days of the experiment (n = 3; means and standard deviation)

4 Conclusion

From the study it can be concluded that the temperature of the pyrolysis and the type of plant material affect the content of the lipid fraction of the organic matter of pyrochar and the concentration of PAHs. Thus, according to the PAH content, the most unfavourable for soil application was pyrochar obtained from the residues of millet (low-temperature pyrolysis), however, at a high pyrolysis temperature, a safe product with the lowest PAHs concentration and a significant lipid fraction is formed. These studies showed that pyrochars can be potentially hazardous to the environment and their production should be carried out under strictly controlled conditions with careful selection of the material and the pyrolysis temperature. In addition, organic substances of pyrochars, by affecting to soil microorganisms, can enhance the emission of carbon dioxide in the initial stages after application, which introduces additional environmental risks of the use of pyrochars.

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References

1. E.Y. Rizhiya, N.P. Buchkina, I.M. Mukhina, A.S. Belinets, E.V. Balashov, Eurasian Soil Sci. **48**, 192–200 (2015)
2. J.W. Gaskin, C. Steiner, K. Harris, K.C. Das, B. Bibens, Am. Soc. Agricultural Biological Engineers **51**, 2061–2069 (2008)

3. J. Lehmann, S. Joseph, *Biochar for Environmental Management: Science and Technology* (Earthscan Publ., London, 2009)
4. A.P. Sinitsyn, A.V. Gusakov, V.M. Chernoglazov, *Bioconversion of lignocellulosic materials* (MSU, Moscow, 1995)
5. B. Maestrini, A.M. Herrmann, P. Nannipieri, M.W.I. Schmidt, S. Abiven, Soil. Biol. Biochem. **69**, 291–301 (2014)
6. C. Wang, Y. Wang, H.M. S.K. Herath, Org. Geochem. **114**, 1–11 (2017)
7. W. Buss, M.C. Graham, G. MacKinnon, O. Mašek, J. Anal. Appl. Pyrol. **119**, 24–30 (2016)
8. J. Wei, C. Tu, G. Yuan, D. Bi, H. Wang, L. Zhang, B.K.G. Theng, B. Environ. Contam. Tox. **103**, 1–6 (2018)
9. H.I. Abdel-Shafy, M.S.M. Mansour, Egypt. J. Petrol. **25**, 107–123 (2016)
10. E. Sagrilo, S. Jeffery, E. Hoffland, T.W. Kuyper, GCB Bioenergy **7**, 1294–1304 (2014)
11. S. Liu, Y. Zhang, Y. Zong, Z. Hu, S. Wu, J. Zhou, Y. Jin, J. Zou, GCB Bioenergy **8**, 392–406 (2015)
12. E.V. Smirnova, K.G. Giniyatullin, A.A. Valeeva, Scientific notes of Kazan University, Natural sciences series **160**, 259–275 (2018)
13. R.V. Okunev, E.V. Smirnova, A.R. Sharipova, I.M. Gilmutdinova, K.G. Giniyatullin, IOP C. Ser. Earth. Env. **107**, 012121 (2018)
14. X. Domene, A. Enders, K. Hanley, J. Lehmann, Sci. Total. Environ. **512–513**, 552–561 (2015)
15. S.E. Hale, J. Lehmann, D. Rutherford, A.R. Zimmerman, R.T. Bachmann, V. Shitumbanuma, A. O'Toole, K.L. Sundqvist, H. Peter, H. Arp, G. Cornelissen, Environ. Sci. Technol. **46**, 2830–2838 (2012)
16. M. Keiluweit, P.S. Nico, M.G. Johnson, M. Kleber, Environ. Sci. Technol. **44**, 1247–1253 (2010)
17. B. Maestrini, P. Nannipieri, S. Abiven, GCB Bioenergy **7**, 577–590 (2015)