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Polycyclic aromatic hydrocarbons concentration in straw biochar with different particle size

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Abstract

Biochar, a carbon-rich material formed by a biomass pyrolyzed at relatively low temperatures (⩽700 °C), showed attractive sorption capacity on both organic pollutants and heavy metals and wildly used in various areas of environmental engineering. However, polycyclic aromatic hydrocarbons (PAHs) may also be assumed to be produced for the oxygen-limited pyrolysis condition in biochar production process. It is not well known about the affect of particle size in concentration and distributing characteristic of PAHs of biochar. In the current study, twenty-seven PAHs concentration in maize straw biochar produced with different powder particle size (9.31, 20.26, 60.77, 71.07, 101.9 μm) were quantified, and the $\sum_{27}$PAHs, total LMW PAHs, total MMW PAHs and total HMW PAHs concentration were analyzed. As the particle size increase, the $\sum_{27}$PAHs concentrations show a trend of firstly increase and then decrease, and the maximum appears at 60.77 μm (166.52 ng/g) and the minimum appears at 101.90 μm (14.63 ng/g). LMW total PAHs and total MMW PAHs concentrations firstly increase and then decrease, with the particle size increasing from 9.31 μm to 101.9 μm. Meanwhile, the total HMW PAH concentrations decrease gradually when biochar particle size increasing. Compared to US, UK background soil concentrations and Canada standards, it is appropriate to conclude that PAHs in straw biochar have minimal effects after application to soil especially at 101.9 μm.

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Keywords: Biochar; PAHs; Maize Straw; Particle size

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1. Introduction

Biochar is the material produced by pyrolysis of biomass in anaerobic or anoxic conditions[1-3]. The common biomass feedstocks to produce biochar are animal excrement, plant waste, crop residues and municipal solid waste such as sludge[3]. Biochar with highly loose and porous structure has the advantage of a large specific surface area. Besides, carboxyl, phenolic hydroxy, anhydride and many other functional groups are contained in its surface [1,3]. As a result, biochar has excellent adsorption performance, and it can strongly adsorb the pollutants in environment and reduce their environmental risks, especially for heavy metals and organic pollutants. Heavy metals and organic pollutants can be strongly adsorbed and accumulated by biochar, and CO_2 in atmosphere can also be immobilized by it. Biochar would be a favorable soil amendment due to its alkalinity and high-carbon content, and when used for soil amendment, it not merely amended the contaminated soil but also improved the soil fertility and slowed down the greenhouse effect. So it is wildly used for soil amendment and to immobilize CO_2 from the atmosphere to the soil [4, 5].Because of those benefits of biochar, it is gaining increasing attention on remediation of heavy metals and organic pollutants, combating climate change, water and wastewater treatment and soil amendment in recent years[6], and it has begun to be produced and used in many regions, for example, in Zimbabwe, 9.9 Mton/yr^{-1} feedstock yield 3.5 Mton/yr^{-1} biochar [7].

However, the potential environmental risks are contained in biochars and cannot be neglected. For example, biochars can immobilize herbicides in unpredictable ways [8]. Most of the metals in feedstock may be concentrated in biochar and this may result in a high metal content biochar [9]. During pyrolysis, organic compounds in feedstock may resolve and then regroup dioxins, furans or polycyclic aromatic hydrocarbon (PAHs) [9-11], especially PAHs. PAHs are ubiquitous pollutants in environment. Volcanic eruptions and forest fires will release PAHs [12], but the main pollution of PAHs result from the industrial process. Sixteen PAHs are classified as Priority Pollutants by US EPA due to their carcinogenic, mutagenic or teratogenic properties [13]. Besides, due to the lipophilic structure of PAHs, PAHs mainly contaminate of soil rather than water [14, 15]. So, PAHs contamination may be caused by biochar production and application to soil. Some studies have already focused on the potential pollutants in biochar, and pyrolysis temperature and feedstock were reviewed as the most important factors affecting the concentration of PAHs in biochar [16, 17]. Marco Keiluweit et al have found that solvent-extractable PAH concentrations in biochars produced at heat treatment temperature of 400 and 500℃ greatly exceed those observed at higher and lower temperature[18]. Sarah E. Hale et al reported that with increasing pyrolysis time and temperature, PAH concentrations generally decreased[8]. But, Ledesma et al showed that large contents of PAHs are produced at temperature greater than 700 ℃[19]. Richard S.Quilliam et al have found that soil contained biochar for 3 years had significantly higher levels of PAH compared to unamended soil[15]. But Alessia Freddo et al [9] and Katja Wiedner et al demonstrated that PAHs associated with biochar following its application to soil are likely to be minimal[20].

To our knowledge, there were little researches focusing on feedstock particle size as influence factor. Different particle size of feedstock may affect the completeness of pyrolysis and the stability of biochar in soil [21]. The relationship between particle size and PAH concentrations is unclear. So, in our paper, straw was chosen as the feedstock and the influence of pyrolysis temperature and straw powder particle size was evaluated.

Straw is an important and wildly used raw material in biochars production. A large number of straws are produced in China every year. Burning was wildly adopted by farmers as an easy and cheap way to remove stalks after harvests, despite the practice being banned by the government. Straw burning brings serious atmospheric pollution and resulting in a waste of resources [22]. Using straw biochar is an ideal recycle technique for waste utilization. But before popularizing straw biochar, it is should be considered that whether the potential pollutants in straw biochar will impact on the environment. For this purpose, our paper focuses on the concentrations of PAHs in straw biochar influence by pyrolysis particle size.

Here introduce the paper, and put a nomenclature if necessary, in a box with the same font size as the rest of the paper. The paragraphs continue from here and are only separated by headings, subheadings, images and formulae. The section headings are arranged by numbers, bold and 10 pt. Here follows further instructions for authors.

2. Materials and Methods

Oxygen-limited pyrolysis was used to produce biochar[4]. Five different particle sizes (d_{50}=9.31 μm, d_{50}=20.26 μm,

d_{50}=60.77 μm, d_{50}=71.07 μm, d_{50}=101.9 μm) of straw powder were prepared by hierarchical impact mill. Those straw powders were compacted in crucible and carbonized by muffle at 350 ℃. The heating rate was 50 ℃·min^{-1} and the holding time was 6 hours. Biochar samples prepared through the method above are marked as MS-9.31, MS-20.26, MS-60.77, MS-71.07, MS-101.9.

PAHs in biochar were extracted with 25 mL hexane/acetone mixture using a microwave accelerated system (CEM Mars Xpress, USA), purification and analyzed by a gas chromatography with a mass spectrometer (Agilent GC6890-MS 5973, USA) in the Laboratory for Earth Surface Processes, Peking University[23]. Detailed information about laboratory PAH analysis can be found in previous publications. Briefly, the extraction solution was concentrated and transferred to a silica/alumina gel column for cleanup. The column was eluted with 20 mL hexane (discharged) and then a 70 mL hexane/dichloromethane mixture. The eluate was then concentrated to 1 mL, spiked with international standards and ready for GC-MS analysis. A HP-5MS capillary column was used. The temperature program is held at 50 °C for one min, increased to 150 °C at a rate of 10 °C/min, to 240 °C at 3 °C/min, and then to 280 °C held for another 20 min. PAHs were identified based on retention time and selected ions in selected ion monitoring mode.

All solvents used were re-distillated and checked for PAHs blank. The silica gel and alumina were baked at 450 °C for 6 h, activated at 300 °C for 12 h, and deactivated with deionized water (3 %, w/w) prior to use. The anhydrous sodium sulfate was baked at 450 °C for 8 h. All glassware was cleaned in an ultrasonic cleaner and baked at 500 °C for at least 10 h. Instrumental detection limits, method detection limits and recoveries from spiked standards were determined in preliminary experiments. The recoveries were all in the acceptable range (70%-130%). Laboratory blanks were measured and subtracted from the sample results. Results reported here are not corrected for recoveries.

3. Results

3.1.Concentrations of PAH in biochar influence by particle size

Concentrations of PAH in five biochar (MS-9.31, MS-20.26, MS-60.77, MS-71.07, MS-101.9) were listed in table 1. As the particle size increases, the $\sum_{27}$PAH concentrations showed a trend of firstly increase and then decrease. From 9.31 μm to 20.26 μm, the $\sum_{27}$PAH concentration dramatically increased from 69.91 ng/g to 148.11 ng/g; when the particle size continue increases to 60.77 μm, the $\sum_{27}$PAH concentration slowly increased to a maximum 166.52 ng/g. After that, when the particle size continue increases to 101.90 μm, the $\sum_{27}$PAH concentration dramatically decreased to a minimum 14.63 ng/g. It seems that biochar derived from the larger diameter raw maize straw has lower potential environmental risk. Besides, the $\sum_{27}$PAH concentrations range (14.63 ng/g ~ 166.52 ng/g) were far below the concentrations reported in reference [8] and [11] in average.

The concentrations of ACY, ACE, FLE, PHE, ANT, FLA, PYR, BaA, CHR, RET, BaP, BeP, BcP were firstly increase and then decrease along with the particle size increases. Here, the maximum of PHE, CHR, BaP, BeP were appeared in 20.26 μm while others were appeared in 60.77 μm. The concentrations of BbF, BkF, PER, IcdP, BghiP, CcdP were decreased gradually but not strictly as the particle size increases, because the concentrations of BbF, BkF, PER, IcdP, BghiP all showed a little rise at 60.77 μm or 71.07 μm. Besides, CcdP has not been detected when particle size is greater than 9.31 μm, and DahA, dBaeP, dBahP, dBacP, dBalP, dBaeF, Cor, dBaiP did not appear in those biochars with five different particle sizes. The minimum of all PAHs were appeared in 101.9 μm, this was further proof that the larger diameter raw maize straw has lower potential environmental risk.

Table 1. Concentrations of PAH in biochar at different particle size.

Compounds		Concentration of PAHs (ng/g) with different particle size(d_{50}, μm) of biochar				
		9.31	20.26	60.77	71.07	101.9
ACY	acenaphthylene	0.00	1.04	1.39	1.30	0.32
ACE	acenaphthene	3.15	7.17	12.45	8.96	0.00
FLE	fluorene	5.66	18.93	23.46	17.67	1.68

PHE	phenanthrene	20.81	58.15	57.25	41.66	4.43
ANT	anthracene	0.98	2.62	4.01	1.82	0.21
FLA	fluoranthene	4.87	12.58	0.00	7.69	1.20
PYR	pyrene	5.97	12.00	18.11	8.34	0.85
BaA	benzo(a)anthracene	2.18	3.38	4.35	2.92	0.70
CHR	chrysene	6.89	14.76	13.36	13.76	2.20
RET	retene	6.22	8.03	21.33	7.98	1.80
BbF	benzo(b)fluoranthene	3.33	2.97	3.01	3.42	0.52
BkF	benzo(k)fluoranthene	2.91	0.94	0.87	0.98	0.15
PER	perylene	0.38	0.15	0.21	0.16	0.00
BaP	benzo(a)pyrene	1.30	1.59	1.34	1.56	0.23
BeP	benzo(e)pyrene	2.17	2.19	2.04	1.88	0.34
IcdP	indeno(1,2,3-cd)pyrene	0.86	0.70	0.81	0.82	0.00
DahA	dibenzo(a,h)anthracene	0.00	0.00	0.00	0.00	0.00
BghiP	benzo(g,h,i) perylene	1.66	0.91	0.96	0.96	0.00
dBaeP	di-benzo(a,e)pyrene	0.00	0.00	0.00	0.00	0.00
dBahP	di-benzo(a,h)pyrene	0.00	0.00	0.00	0.00	0.00
BcP	benzo(c)phenanthrene	0.00	0.00	1.57	1.14	0.00
CcdP	cyclopenta(c,d)pyrene	0.57	0.00	0.00	0.00	0.00
dBacP	di-benzo(a,c)pyrene	0.00	0.00	0.00	0.00	0.00
dBalP	di-benzo(a,l)pyrene	0.00	0.00	0.00	0.00	0.00
dBaeF	di-benzo(a,e)fluoranthene	0.00	0.00	0.00	0.00	0.00
Cor	coronene	0.00	0.00	0.00	0.00	0.00
dBaiP	di-benzo(a,i)pyrene	0.00	0.00	0.00	0.00	0.00
Total concentration		69.91	148.11	166.52	123.02	14.63

3.2.Distribution characteristics of PAH in biochar influence by particle size

The concentrations of LMW, MMW and HMW PAH in biochar at different particle sizes were shown in figure 1. As the particle size increases, the total LMW PAHs and total MMW PAHs concentrations were firstly increase and then decrease, while the total HMW PAHs concentrations were falling slowly. At 9.31 μm, the total LMW PAHs concentration was 36.82 ng/g at first and then increased dramatically to 95.94 ng/g at 20.26 μm and then increased slowly to a maximum 119.89 ng/g at 60.77 μm. As the particle size continue increases to 101.90 μm, the total LMW PAHs concentration decreased to a minimum 8.44 ng/g. The total MMW PAHs concentration was 20.48 ng/g at 9.31

μm and then showed a maximum 42.72 ng/g at 20.26 μm, then decreased slowly to a minimum 4.95 ng/g at 101.9 μm. The total HMW PAHs concentrations decreased slowly from 12.61 ng/g at 9.31 μm to 1.24 ng/g at 101.9 μm. In the scope of our study, the concentrations of LMW PAH were much higher than the MMW and HMW PAH. Besides, the greater the particle size, the smaller the concentration, this greatly reduces the harm to human and environment.

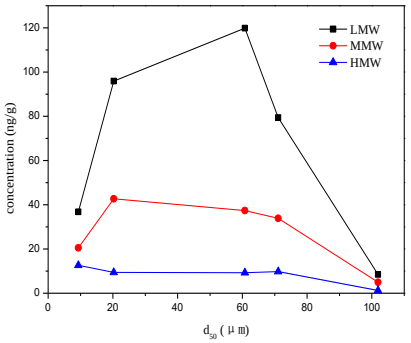

Figure 1. The concentrations of total LMW, MMW and HMW PAHs in biochar at different particle size

As before, PAHs with the top three content were set as examples and their distribution were analyzed. As table 1 shows, at 9.31 μm, PAHs with the top three content were PHE, CHR, RET and their concentrations were 20.81 ng/g, 6.89 ng/g, 6.22 ng/g respectively. The percentage of total concentration was 48.52%. At 20.26 μm, PAHs with the top three content were PHE, FLE, CHR and the percentage of total concentration was 62.01%. At 60.77 μm, PAHs with the top three content were PHE, FLE, RET and their concentrations were 57.25 ng/g, 23.46 ng/g, 21.33 ng/g. The percentage of total concentration was 61.28%. At 71.07 μm, PAHs with the top three content were PHE, FLE, CHR and their concentrations were 41.66 ng/g, 17.67 ng/g, 13.76 ng/g. The percentage of total concentration was 59.41%. At this particle size, the concentration of PHE was 2.36 times of FLE and triple of CHR. At 101.90 μm, PAHs with the top three content were PHE, CHR, RET and their concentrations were 4.43 ng/g, 2.20 ng/g, 1.80 ng/g. At this particle size, their (PHE, CHR and RET) concentrations reduced greatly compared to the concentrations at other particle size. The percentage of total concentration was 57.62%, which was still high because the other PAH concentrations were also reduced greatly. The concentration of PHE was always the highest in each particle size as well as the rangeability that increased from 20.81 ng/g at first to a maximum 58.15 ng/g and then decreased to a minimum 4.43 ng/g in the end. It showed a trend of firstly increase and then decrease along with the increase of particle sizes. Other high level PAHs were CHR, FLE, RET et al. This demonstrates that PHE and other low molecular weight PAHs are commonly found in biochar with less limited by particle size.

4.Discussion

PAHs released into the atmosphere from natural and industrial pyrolysis process are returned to the ground surface by atmospheric deposition process and contributing to the PAH concentrations of soils [24]. A soil quality investigation [25] reported US soil $\sum_{16}$PAH (the same as our paper) concentrations range between 1520 ng/g and 662000 ng/g with soil samples were taken at the depth 0.2 feet below ground surface. Jones et al (1989) [26] reported that UK soil $\sum_{14}$PAH concentrations in rural and urban areas range between 100 ng/g and 54500 ng/g. A document of NOVA SCOTIA Canada [27] is shown factional in table 2.

Table 2 References for Pathway Specific standards – Agricultural Soil (ng/g)

Parameters	Agricultural Land Use Human Receptor Pathways	Agricultural Land Use Ecological Receptor Pathways
NAP	1800	0.6

No-Carcinogenic PAH compounds	ACE	5300	/
	ACY	78	/
	ANT	24000	2.5
	FLA	3500	50
	FLE	2700	/
	PHE	/	6.2
	PYR	2100	/
Carcinogenic PAH compounds	BaA	/	0.63
	BaP	/	20
	B(b,j,k)F isomers	/	9.5
	BghiP	/	8.3
	CHR	/	8.8
	DahA	/	/
	IcdP	/	0.48

According to results of the current study, the biochar $\sum_{15}$PAH concentrations range between 12.49 and 141.37ng/g, and the $\sum_{LMW}$PAH concentrations range between 6.64 and 98.56 ng/g, and the $\sum_{MMW}$PAH concentrations range between 4.95 and 42.72 ng/g, and the $\sum_{HMW}$PAH concentrations range between 0.9 and 10.06 ng/g.

Comparing to the concentrations of $\sum_{16}$PAH in US soils and $\sum_{14}$PAH in UK soils, it is appropriate to conclude that PAHs in straw biochar have minimal effects after application to soil. Compared to the Canada standards, the biochar $\sum_{LMW}$PAH concentrations are also likely to be minimal impact on human and ecological receptor at any temperatures and particle sizes. But the biochar $\sum_{MMW}$PAH and $\sum_{HMW}$PAH concentrations are likely to be minimal impact at 101.9 μm.

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