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Application of biochar to soils may result in plant contamination and human cancer risk due to exposure of polycyclic aromatic hydrocarbons

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ABSTRACT

Biochars are added to soil to improve agronomic yield. This greenhouse- and field-scale study evaluated polycyclic aromatic hydrocarbon (PAH) contamination in 35 commercial and laboratory-produced biochars, and assessed the effects of biochar amendment of soils on PAH accumulation in vegetables and the risk for cancer. The total and bioavailable PAH concentrations in biochars varied from 638 to 12,347 μg/kg and from below the detection limit (BDL) to 2792 μg/kg, respectively. PAH formation in biochars decreased with increasing production temperature (350–650 °C). Root exudates enhanced PAH release from biochars. The total PAH concentrations in eight edible vegetables growing in biochar-amended soil varied according to biochar and vegetables type from BDL to 565 μg/kg. A health risk assessment framework was integrated with the benzo[*a*]pyrene toxic equivalency quotient and the incremental lifetime cancer risk (ILCR) to estimate the exposure risk for human beings via ingestion of PAH-contaminated vegetables. The total ILCR for adults was above 10^{-6}, which suggests a risk to human health from direct exposure to PAHs in vegetables grown in biochar-amended soil. These results demonstrate that biochar application may lead to contamination of plants with PAHs, which represents a risk to human health. The PAH levels in biochars produced using different conditions and/or feedstocks need to be evaluated and biochars should be pretreated to remove PAHs before their large-scale agronomic application.

1. Introduction

Approximately 140 billion metric tons of agricultural residues are produced per year worldwide, with 800 million tons in China (United Nations Environmental Program, 2010; Fu et al., 2017). How to reuse this agricultural waste is an important issue. The application of biochar derived from crop residues via thermal pyrolysis to land facilitates nutrient cycling and is increasingly important for agricultural sustainability for a growing population. According to the State of the Biochar Industry Report of the International Biochar Initiative (IBI, 2017), up to 800,000 tons of crop residues were converted into biochar from 2016 to 2017 in China, which is expected to increase to 3 million tons within five years.

The application of biochar to soil is a new approach to reusing crop straw. Biochar is a low-cost and environmentally friendly agent that increases crop productivity and reduces soil pollution. A 3-year field trial found a significant increase (3.0 t/ha) in the above-ground biomass of *Dactylis glomerata* growing in a field amended with biochars derived from mechanically chipped trunks and large branches pyrolyzed at 450 °C for 48 h (Jones et al., 2012). Similarly, amendment with biochar pyrolyzed from wheat straw at 10 and 40 t/ha enhanced rice yields by 12% and 14% on the Tai Lake Plain, China (Zhang et al., 2010). Moreover, biochar may decrease the bioavailability of toxic elements and organic compounds in contaminated soils and thus reduce their accumulation in crops (Khan et al., 2014; Lehmann, 2007; Herath et al., 2013). Khan et al. (2014) observed that adding biochar (10%) to soil markedly reduced the accumulation of As(III) (72%), dimethylarsinic acid (DMA) (74%), and As(V) (62%) in rice. In another study, adding peanut shell-based biochar (5%) to soil significantly decreased (84%) PAH accumulation in turnip (Khan et al., 2015a). However, most studies did not assess the risk of contamination due to biochar application.

Biochar may be produced from different biomass such as manure, crop residue, sludge, wood, etc. by thermal pyrolysis (Lehmann, 2007). However, PAHs are produced during pyrolysis (carbonization) in the

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absence of air. Biochars produced by pyrolysis at different temperatures and from different feedstocks may contain different levels of PAHs. Hilber et al. (2012) reported that the total concentrations of 16 United States Environmental Protection Agency (US-EPA)-priority PAHs in four biochars ranged from 9113 μg/kg (coniferous residues) to 355,295 μg/kg (wood residues). In a previous study, the total concentrations of 11 three- to five-ring PAHs in grass (tall fescue straw)- and wood (ponderosa pine)-derived biochars produced at 400 °C and 500 °C were 130–26,000 and 50–30,200 μg/kg, respectively (Keiluweit et al., 2012). In another study, the total PAH level in biochar produced by thermal pyrolysis of birchwood was10,000 μg/kg (Fagernäs et al., 2012). Hence, biochar used as a soil amendment agent may act as a source of PAHs (Mukherjee and Lal, 2014; Qadeer et al., 2017). Biochar amendment of soils reportedly also has adverse effects (Mukherjee and Lal, 2014; Kuppusamy et al., 2016). Rombolà et al. (2012) reported that the total PAH concentrations in soil amended with orchard pruning-derived biochars were 34,500–42,900 μg/kg. Biochar amendment led to a marked increase in the total extractable PAH concentrations, which subsequently decreased from 153 to 78 μg/kg after 35 months. These PAH concentrations were significantly higher than that of unamended control soil (24 μg/kg). Similarly, Quilliam et al. (2013) found that the concentrations of 16 US-EPA-priority PAHs in soil amended with wood-based biochar (50 t/ha) for 3 years was 1953 μg/kg, significantly higher than that of control soil (1131 μg/kg).

PAHs are carcinogenic and mutagenic, and thus are classified as persistent organic health-threatening pollutants (Perera, 1997). The application of PAH-containing biochar to agricultural soil may represent a risk to human health, as vegetables may accumulate PAHs at high concentrations from such soils (Gao and Collins, 2009). Hence, an understanding of the negative effects of PAH-containing biochars on crop security and human health is critical for their large-scale application. To date, research has focused on the effects of biochar on crop productivity; there is little information on the risk of vegetable contamination and risk to human health. Although soil PAH levels are reportedly increased by biochars (Quilliam et al., 2013), to the best of our knowledge, few studies have investigated PAH accumulation in vegetables and the risk for human cancer due to biochar amendment of agricultural soil.

To address this crucial knowledge gap, we conducted greenhouse and field experiments to: (1) elucidate the PAH accumulation in vegetables grown in biochar-amended soil; and (2) estimate the incremental lifetime cancer risk (ILCR) via dietary intake of vegetables contaminated with biochar-associated PAHs in soil.

2. Materials and methods

2.1. Chemicals, soil, and biochar

A standard solution of the 16 EPA-priority PAHs (98% purity) was purchased from O2si Smart Solutions Co. (Charleston, SC). The properties of those PAHs are listed in Table S1.

The Typic Paleudalf soil used for the greenhouse experiments was collected from Nanjing, China, and has the following physicochemical characteristics: pH 6.14, 15.5 g/kg total organic carbon content, 1.1 g/kg total nitrogen content, 24.7% clay, 13.4% sand, and 61.9% silt. Soil pH was determined by agitating the mixture of soil: distilled water (1:2.5) for 30 min and then standing quietly for 1 h. The pH of supernatant was measured by a pH meter. The total organic carbon content was measured using the potassium bichromate titrimetric method according to National Standards of China (GB 9834-88). The total nitrogen content was determined using an automatic Kjeldahl nitrogen meter (SKD-1000, Shanghai, China). After collection, the soil was air-dried and sieved (< 4 mm). The field experiment was performed in suburban agricultural fields in Nanjing, and the soil was classified as a typic Paleudalf. The characteristics of the field soil are as follows: pH 6.84, 8.5 g/kg total organic carbon content, 2.3 g/kg total nitrogen content, 24.4% clay, 12.1% sand, and 63.5% silt. The initial concentrations of PAHs in test soils for greenhouse and field experiments were under the detection limits.

Twenty biochars were purchased at a market and had been produced by pyrolysis at 250–900 °C from apple wood (B1), elm wood (B2), lychee tree (B3), oak tree (B4), walnut shell powder (B5), coconut husk (B6), pine wood (B7), jujube wood (B8), corn stover (B9), wheat straw (B10), pear tree (B11), rice straw (B12 and B13 in Nanjing in 2016 and 2017; B14 in Liyang), rice husk (B15, B16, and B17 in Nanjing, Shanghai, and Nantong, respectively), and bamboo (B18, B19, and B20 from Zhejiang, Guangxi, and Jiangxi, respectively).

To assess the effects of feedstock and pyrolysis temperature on PAH concentrations in biochar, 15 biochars were produced in our laboratory. The feedstocks and pyrolysis temperatures used were as follows: reed (B21, B22, and B23 produced at 350 °C, 500 °C, and 650 °C, respectively); sesame stalks (B24, B25, and B26 produced at 350 °C, 500 °C, and 650 °C, respectively), pine needles (B27, B28, and B29 produced at 350 °C, 500 °C, and 650 °C, respectively), soybean straw (B30, B31, and B32 produced at 350 °C, 500 °C, and 650 °C, respectively), and cypress wood (B33, B34, and B35 produced at 350 °C, 500 °C, and 650 °C, respectively). All of these biochars were produced by pyrolysis in muffle furnace under an oxygen-free condition. The heating rate was employed at 5 °C/min, and kept for 8 h when reaching the set temperature (350 °C, 500 °C, and 650 °C).

The general physicochemical properties of the commercial and laboratory-produced biochars are listed in Table S2 and Figs. S1 and S2 in Supporting information (SI).

2.2. Greenhouse and field experiments

Each commercial biochar was manually mixed with the test soil at a 3% ratio, corresponding to 48 t/ha (assuming a soil depth of 30 cm and density of 1.2 g/cm^3). Each cell of eight-cell potted containers (Fig. S3 in SI) was filled with 1 kg biochar-mixed soil, irrigated with deionized water, allowed to stand for 1 day, and planted with seedlings of carrot (*Daucus carota*), Chinese cabbage (*Brassica chinensis*), water spinach (*Ipomoea aquatica Forsk*), pterocladia tenuis (*Brassica rapa*), spinach (*Spinacia oleracea*), pakchoi (*Brassica campestris*), lettuce (*Cichorium endivia*), or cherry radish (*Raphanus sativus*). To produce seedlings, plant seeds were soaked in warm water (55–60 °C) for 15 min and transferred to Petri dishes in a 28 °C incubator for 3 days to germinate. The containers were placed in random locations in the greenhouse at 25 ± 3 °C (day) and 20 ± 3 °C (night), with 12 h of natural light, until reaching maturity. Each cell contained 8 seedlings. Half-strength Hoagland's nutrient solution (2 mL) was added to each cell once for the first 2 weeks; subsequently, full-strength Hoagland's nutrient solution (50 mL) was added to each cell once weekly until harvest. Each experiment was conducted in triplicate. Chinese cabbage, water spinach, pterocladia tenuis, spinach, pakchoi, and lettuce were harvested after 45 days, and carrot and cherry radish were harvested after 70 days. The photos of test plants in greenhouse experiments were shown in Fig. S4 in SI. The harvested plants were separated into shoot and root parts, and thoroughly washed with deionized water, freeze-dried, and pulverized. Soil samples were collected from each cell, freeze-dried, and passed through 2 mm sieves. Plant and soil samples were stored at −20 °C until analyses.

The field experiment was performed in suburban agricultural fields in Nanjing, China using the B2, B5, B7, B9, B16, B18, B31, and B34 biochars. The field experiment was of randomized design, involving eleven 2 × 2 m^2 plots. The biochars were manually mixed with the field soil at a 3% ratio, corresponding to 48 t/ha (assuming a soil depth of 30 cm and density of 1.2 g/cm^3). Base fertilizer comprising 176 g N, 39 g P, and 61 g K was added to each plot. Two vegetables, namely, Chinese cabbage (*Brassica chinensis*) and pakchoi (*Brassica campestris*), were grown in each plot. During the growth period, the plots were irrigated with water every 2 days, and plant samples were collected after