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# Bioavailability assessment of thiacloprid in soil as affected by biochar

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## HIGHLIGHTS

- Effects of BC500 on the degradation and sorption of thiacloprid were investigated.
- Effects of BC500 on the bioavailability of thiacloprid in soils were investigated.
- Tenax method predicted the bioavailability of thiacloprid accurately in soils.
- BC500 enhanced the bioaccumulation of thiacloprid in the aged soils.

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## ABSTRACT

Biochars can significantly sorb pesticides, and reduce their bioavailability in agricultural soils. In this study, the effects of a type of biochar (BC500) on the sorption, degradation, bioaccumulation and bioavailability of thiacloprid, which is a commonly used insecticide, were investigated. The thiacloprid sorption constant ($K_f$ values) increased by 14 times after 2% BC500 application, and the degradation of the insecticide decreased with increasing amounts of the biochars in the soil. Coupled with the exhaustive extraction and single-point Tenax method, the bioavailability of thiacloprid was predicted in the presence of the biochar. In soils amended with BC500, the thiacloprid concentrations accumulated in Tenax correlated well with those observed in earthworms ($R^2 = 0.887$), whereas the concentrations extracted by exhaustive method followed a less significant relationship with those in earthworms ($R^2 = 0.624$). The results of Tenax extractions and earthworm bioassays indicate that biochar reduces the bioavailability of thiacloprid in soil, but the delayed degradation and increased earthworm accumulation in aged biochar-amended soil imply that the environmental risks of biochar application to earthworms remain.

## 1. Introduction

Thiacloprid is a new chloro-nicotine type insecticide for sucking and chewing pests. This insecticide has strong contact, stomach and systemic toxicity on target organisms. In recent decades, thiacloprid was progressively applied as seed dressings and soil additions in a variety of crops, fruits and vegetables, and its residues could be found in both soil and water (Angioni et al., 2011; Blacquiere et al., 2012). The pesticide residues in the soil may cause long-term bioaccumulation and pose potential risks to organisms in the environment. Several studies reported that thiacloprid could cause delayed lethal effects on freshwater arthropods at low concentrations and it also could negatively affect the foraging behavior of bees (Beketov and Liess, 2008; Mommaerts et al., 2010). Recently, most studies about thiacloprid focused on the toxicity and long term effects to aquatic organisms (Beketov and Liess, 2008; Beketov et al., 2008), but systematic studies about the environmental behavior and countermeasures to remedy the pollution of thiacloprid in soil remain limited. Therefore, the development of countermeasures to remedy of the pesticide-contaminated environment, particularly soil, is of great significance to reduce the risks posed by the bioaccumulation of thiacloprid.

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*Abbreviations:* BC500, biochar produced from magnolia trees at 500 °C under limited oxygen in a muffle furnace; UPLC-MS/MS, ultrahigh-performance liquid chromatography-tandem mass spectrometry; ASE, accelerated solvent extraction; BSAF, biota-soil accumulation factor; DOC, dissolved organic carbon.

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Because of its tremendous specific surface area (SSA), high microporosity and other physiochemical properties, biochars have been shown to be particularly effective in the sequestration of organic contaminants and pesticides to reduce their risks in soils (Gong et al., 2016; Jin et al., 2016; Kong et al., 2011; Mesa and Spokas, 2011; Oleszczuk et al., 2012; Wang et al., 2013; Yu et al., 2006; Zheng et al., 2010; Martin et al., 2012). For example, Martin et al. (2012) showed that the application of fresh biochars to soil significantly increased the sorption capacity of the soil for atrazine and diuron compared to the control soil, and the sorption–desorption hysteresis was prominent in the soil amended with fresh biochar. Yu et al. (2011) found that the amendment of biochar to soils could significantly increase the sorption of acetamiprid, and the dissipation of acetamiprid in soils that were amended with biochar was delayed compared to that in soils without biochar amendment. And Sopeña and Bending (2013) reported that a type of biochar had no effect on the degradation of azoxystrobin. Butfor pesticides with slow degradation rates, such as methyl isothiocyanate, the application of a biochar can accelerate its degradation (Fang et al., 2016). Because pesticides have different physiochemical properties, the biochar amendment may have diverse effects on environmental behavior of pesticides in soil. For compounds that are easily degradable and strongly hydrophilic, like neonicotinoid insecticides, the effects of biochar on the degradation and bioavailability must be further investigated.

Measuring the bioavailable fraction of soil contaminant in biochar-amended soils is an important step to predict the bioavailability of the contaminants and to assess the effects of biochars on living organisms. A direct assessment of the pesticide toxicity using relevant organisms can provide reliable data but the assays are often time-consuming and relatively costly. It is well documented that solid-phase microextraction (SPME) and Single-point Tenax extraction are two representative procedures to predict the bioavailability across diverse pollutants (Paumen et al., 2008; Brennan et al., 2009; Harwood et al., 2012; van Noort et al., 2014). SPME was effectively used in predicting the bioavailability of HOC water and sediment (Paumen et al., 2008; Brennan et al., 2009). However, HOCs often take a long time to reach equilibrium between the SPME fiber and the matrix. Furthermore, SPME uptake processes may be affected by various environmental factors, such as the temperature and salinity (You et al., 2011). Comparatively, Tenax extractions are rapid (24 h is the accepted duration for Single-point extraction), and robust (satisfactory correlations between Tenax-extractable concentrations and tissue concentrations have been established by many studies, and their correlations are uniform across species in some examples.) (Harwood et al., 2015). Considering that thiacloprid is a contaminant that rapidly degrades and soil is a relatively complicated matrix, Single-point Tenax extraction was selected to predicting the bioavailability of thiacloprid in soils with biochar.

The objectives of this study were (i) to investigate the effects of the biochar (BC500) amendment on the sorption and degradation of thiacloprid in soils with different BC dosages, (ii) to evaluate the accuracy of Tenax extraction methods to assess the bioavailability of pesticides in soil with different biochar application rates, (iii) to investigate the effects of the biochar (BC500) amendment on the bioavailability of thiacloprid to earthworms.

## 2. Materials and methods

### 2.1. Chemicals

Analytical-grade thiacloprid (99.0% chemical purity) was purchased from Qinchengyixin Technology Co. Ltd. (Beijing, China). Log $K_{ow}$ (Octanol-water partition coefficient at pH 7, 20 °C) of thiacloprid was 1.26. The stock solution of thiacloprid (1000 mg/L) was prepared by dissolving the weighed insecticide in HPLC-grade acetonitrile (>98.0% purity). Analytical-grade sodium azide and calcium chloride and all solvents of high-performance liquid chromatography (HPLC) grade were obtained from Beihua Finechemicals Co. (Beijing, China).

### 2.2. Biochar and soils

An agricultural soil sample was collected from a planting base in Beijing, China. The soil was sampled from the upper 20 cm, passed through a 2 mm sieve for the degradation and bioaccumulation experiment. The soil sample was stored at 4 °C for about two months before use. The selected physicochemical properties of the soil are shown in Table 1. The soil physico-chemical properties were analyzed by conventional standard procedures (Lu, 2000).

The biochar was produced from magnolia trees (*Magnolia denudata*). Briefly, air-dried magnolia tree woodchips in crucible were pyrolyzed at 500 °C under limited oxygen in a muffle furnace. The reactor was first purged with nitrogen for 10 min, heated to a 500 °C with a heating rate of 15 °C/min and held for 3 h under nitrogen atmosphere. The obtained samples were washed with deionized water to remove excessive water-soluble inorganics and dried at 80 °C for 24 h (Chen and Huang, 2011; Gong et al., 2016). Then the prepared biochar was ground to a fine powder using a mortar and a pestle and passed through a 2 mm sieve. In our study, the biochar, which was pyrolyzed at 500 °C was named BC500. The physic-chemical properties of BC500 are listed in Table 1. The specific surface area (SSA) of the biochars was determined using the V-Sorb 2800P surface area and pore distribution analyzer (Gold APP Instruments Corporation, China). The elemental composition was measured using a CHN element analyzer (vario PYRO cube, Elementar Analysensysteme GmbH, Germany).

Biochar (BC500) amended soils used in the experiment were set at 1, 5, 10, and 20 g biochar $kg^{-1}$ soil. The soils in the sorption and degradation experiments were dried before mixing with the biochar. The soils were thoroughly mixed on a rotary shaker for 2 d before their use as sorbents for the sorption and soil degradation experiments.

### 2.3. Sorption experiments

To compare the sorption affinities of five types of soils with different biochar application ratios (0, 0.1%, 0.5%, 1%, and 2%), the thiacloprid sorption experiments were conducted using the batch equilibration technique as described in many other studies (Yang and Sheng, 2003a; Zhang et al., 2010). We weighed 5 g soil into a 50 mL centrifuge tube; then, the soils were suspended in 25 mL of 0.01 M $CaCl_2$ solutions (containing 0.1% $NaN_3$ to inhibit the microbial activity) The final spiked concentrations in the centrifuge

**Table 1**
Physico-chemical properties of soil and biochar.

| | Soil | Biochar |
|---|---|---|
| pH | 6.86 | 9.39 |
| Organic matter (%) | 1.23 | –[a] |
| Total C (%) | 0.77 | 76.17 |
| Total N (%) | 0.194 | 0.99 |
| Total O (%) | – | 14.35 |
| Clay (%) | 3.21 | – |
| Silt (%) | 33.56 | – |
| Sand (%) | 61.23 | – |
| Specific surface area ($m^2g^{-1}$) | – | 26.3 |
| Pore width (nm) | – | 5.34 |

[a] (–) not determined.