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Polyoxymethylene passive samplers to assess the effectiveness of biochar by reducing the content of freely dissolved fipronil and ethiprole

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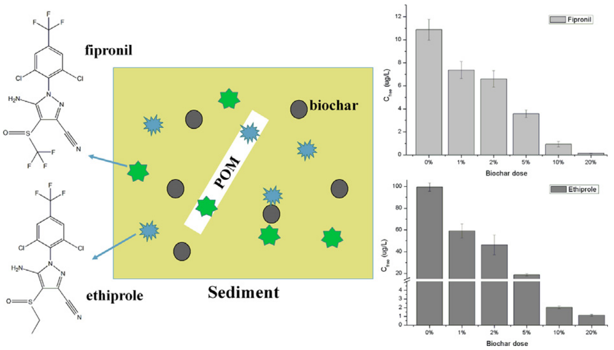
HIGHLIGHTS

- POM was used to determine the freely dissolved fipronil and ethiprole.
- Sorption capacity of biochar increased with the increase of pyrolytic temperature.
- Magnolia biochars reduced the freely dissolved fipronil and ethiprole in sediments.
- Sorption capacity of biochar is related to the dosage, aging time and sediment type.

GRAPHICAL ABSTRACT



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ABSTRACT

An equilibrium passive sampler based on polyoxymethylene (POM) was used to determine the freely dissolved concentrations (C_{free}) of fipronil and ethiprole. The sorption equilibrium times of fipronil and ethiprole in POM were 14.2 d and 24.0 d, respectively. The POM-water partitioning coefficients ($\log K_{POM\text{-}water}$) were 2.6 for fipronil and 1.4 for ethiprole. The method was further used to evaluate the sorption behavior of biochars which produced by pyrolysis of Magnolia wood (*Magnolia denudata*) at 300 °C, 500 °C and 700 °C. The amounts of target compounds adsorbed increased with increasing pyrolysis temperature of the biochars. Biochars characterized by a low polarity index had better sorption capacity for the target compounds. The additions of biochars to sediment were effective in reducing C_{free}, and the enhancement was found to be more pronounced with high biochar content. C_{free} in sediment with more organic matter was significantly higher after biochar addition. Increasing the sediment-biochar contact time from 7 to 30 d resulted in an increase in sorption of the compounds. We conclude that Magnolia wood biochar effectively reduces the content of freely dissolved fipronil and ethiprole content in sediment.

1. Introduction

Fipronil (5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-(trifluoromethanesulfinyl)-1H-pyrazole-3-carbonitrile) and ethiprole

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(5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-(ethanesulfinyl)-1H–pyrazole-3-carbonitrile) are a class of phenylpyrazole insecticide. Ethiprole differs from fipronil only by a single substituent, and therefore they have similar potency in many aspects (e.g., photochemistry, action at the GABA receptor and insecticidal potency) (Caboni et al., 2003). Fipronil and ethiprole pose a high risk to aquatic organisms, bees, silkworm, birds and even humans. Fipronil can cause damage to the kidneys, liver and thyroid glands, as reported by the World Health Organization (WHO). Recently, the incident of the fipronil contaminated eggs which happened in Europe and Asia has attracted wide public concern in the world and millions of chicken eggs have been pulled from supermarket shelves. Furthermore, studies have demonstrated that fipronil can contaminate aquatic environments, where its concentration is up to 25,400 ng/L (water column) (Yang et al., 2010a) and 630 ng/g (bed sediment) (Hintzen et al., 2009). Such contamination poses a threat to the vitality of underground organisms and other organisms. Indeed, the bed sediment is thought to be the main depository of organic contaminants in aquatic environments, and this constitutes a serious environmental threats (Cui et al., 2010). However, few studies have been carried out on the remediation of these chemicals in sediment (Yang et al., 2010b).

Recently, an in situ technique was proposed as a promising means for managing contaminated sediments sites; the technique is based on the treatment of sediment with carbonaceous materials having a high affinity for organic contaminants, thereby providing an opportunity for carbon sequestration (Chai et al., 2011; Ghosh et al., 2011). Many studies have documented the effectiveness of this method. For example, Lou et al. reported that biochar prepared from rice-straw has a high sorption capacity for pentachlorophenol, thus decreasing the bioavailability of this chemical in sediment and reducing its negative impact on wheat seed growth (Lou et al., 2011). Khan et al. reported that the addition of biochar to soil reduced bioaccumulation of PAHs and toxic elements (As, Cd, Cu, Pb and Zn) in turnips (*Brassica rapa* L.) (Khan et al., 2015). Yang et al. investigated the influence of biochars prepared from the burning of cotton on the bioavailability of fipronil (Yang et al., 2010b). No such research on ethiprole has been published, because ethiprole is often used as a substitute for fipronil, however, a study of ethiprole is necessary.

Here we studied the sorption capacity of biochar produced by burning Magnolia wood (*Magnolia denudata*), for fipronil and ethiprole. To assess the effectiveness of sediment remediation strategies using biochar, the freely dissolved concentration was introduced at the same time. The freely dissolved concentration is a key parameter in toxicology and environmental chemistry as it is a driving force for the distribution, transport, and bioaccumulation of chemicals (Mackay and Paterson, 1991; Mayer et al., 2000; Reichenberg and Mayer, 2006). It is often considered a good predictor of chemical bioavailability. Therefore, the measurement of freely dissolved concentrations is pivotal for understanding the ecotoxicological risk of chemical in the environment. In this regard, passive samplers can serve as a useful tool and have been developed to indirectly measure the freely dissolved concentrations of pollutants such as polyoxymethylene (POM). POM has an excellent physical stability and a smooth surface, and it consists of a repeated —CH_2—O— polar group that facilitates higher sorption capacity for certain polar compounds compared with some other commonly used equilibrium passive sampler sorbents, e.g., poly(dimethylsiloxane) and low-density polyethylene (Endo et al., 2011; Jonker and Koelmans, 2001). Therefore, we used POM to determine the freely dissolved concentration of fipronil and ethiprole in sediments.

The aims of the present study were as follows: 1) to evaluate the bioavailability of fipronil and ethiprole using the passive sampler, POM, based on measuring their freely dissolved concentration; 2) to evaluate the effectiveness of biochars for reducing the bioavailable fraction of fipronil and ethiprole in sediment; and 3) to assess affecting factors such as biochar preparation temperature, biochar dose, sediment/biochar aging time, and sediment types that impact efficacy.

2. Materials and methods

2.1. Chemicals

LC-grade acetonitrile (MeCN) were obtained from Sigma–Aldrich (Steinheim, Germany). Methanol, acetone, hexane, MeCN and petroleum ether were analytical grade and purchased from Bei-hua Finechemicals Co. (Beijing, China). Sodium azide (NaN_3) produced by Sigma-Aldrich were purchased from Belllancom life sciences and laboratory fine chemicals (Beijing, China).Ultra-pure water was obtained from a Milli-Q system (Bedford, MA, USA). Fipronil (95% purity) was obtained from Zhejiang Heben Pesticide & Chemicals Co., Ltd. (Zhejiang, China). Ethiprole (95% purity) was bought from Adamas Reagent, Ltd. (Shanghai, China) and internal standard flufiprole (96% purity) was obtained from Dalian Raiser Pesticides Co., Ltd. (Dalian, China).

2.2. Materials

Sediment and sewage sludge samples with no contamination history were dredged from a stinking ditch and a reservoir from Haidian District (Beijing, China). The samples were collected from the uppermost 5–10 cm layer of the sediment. The sediments samples were wet-sieved through a 2 mm sieve, freeze-dried under vacuum condition and kept frozen (−20 °C) until use. The sediments samples were defined as S1 and S2, respectively. The total organic carbon (TOC) contents and pH of the S1 and S2 were 40.0 g/kg and 30.2 g/kg, 7.23 and 7.86, respectively.

Magnolia wood (*M. denudata*) was pyrolyzed in a porcelain crucible under oxygen-limited conditions at 300 °C, 500 °C and 700 °C for 4 h in a muffle furnace, and then the samples were sieved with the particles <2 mm. The produced biochars under 300 °C, 500 °C and 700 °C are designated as BC300, BC500 and BC700, respectively. The elemental composition of each biochar was determined with a graphite furnace-atomic sorption spectrometry analyzer (Analytik Jena AG, Germany). Surface area, pore size and volume were measured using V-Sorb 2800P specific surface area and pore size analyzer (Gold APP Instrument Corporation, Beijing). The biochars pH was measured in a mixture of biochar and pure water (1:2.5) using a pH meter. The detailed properties of the three biochars are listed in Table 1.

A commercially available Polyoxymethylene (POM, 76 μm thick) was purchased from CS Hyde Company (Lake Villa, IL). POM sheets were cut into strips of desired weight and washed with hexane (1 day) and methanol (1 day), after which the strips were air-dried before use (Endo et al., 2011).

2.3. Determination of POM-water partitioning coefficients

The experiments were implemented in 250-mL all-glass bottles that were wrapped with aluminum foil to prevent photochemical degradation. The experimental water containing 0.2 g/L sodium azide was adjusted to pH 7 with 10 mM phosphate buffer solution. POM sheets (100 mg) were added into 250-mL all-glass bottles and three replicates were prepared.

The sorption kinetics of fipronil and ethiprole were measured to evaluate the equilibrium time for the target compounds in POM. The experimental system was spiked with a methanol stock solution of fipronil or ethiprole to obtain a final aqueous concentration of 5 μg/L fipronil and 100 μg/L ethiprole. The methanol concentration in water was <0.1% (*v*/v) to minimize the co-solvent effects. Serial sampling was carried out at 1, 3, 7, 14, 21, 28 and 35 d.

Isotherms for sorption of fipronil and ethiprole to POM were conducted to determine the equilibrium partition coefficients of fipronil and ethiprole between POM and water (K_{POM}). The tested batch systems were spiked with 1–2000 μg/L of methanol solutions containing fipronil and ethiprole with methanol contents <0.1% (*v*/v) in water. All bottles were rolled end-over-end in an orbital shaker (Model HCY-DB,