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Pollutant and Soil Types Influence Effectiveness of Soil-Applied Absorbents in Reducing Rice Plant Uptake of Persistent Organic Pollutants

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ABSTRACT

Persistent organic pollutants (POPs) in soils are an environmental concern due to their long-term bioavailability, which could be reduced by adding adsorbents. However, testing of these adsorbents is necessary prior to widespread field application. The effects of three adsorbents, nano-organic montmorillonite, nano-organic silicon dioxide (SiO_2), and activated carbon, on hexachlorobenzene (HCB) and pentachlorobenzene (PeCB) accumulation in rice (*Oryza sativa* L.) plants were tested in a greenhouse experiment using two soils, a Hydragric Acrisol (Ac) and a Gleyi-Stagnic Anthrosol (An). The bioconcentration factors (BCFs) of HCB and PeCB to rice roots were 2.3–3.7 and 2.0–3.0 times those to rice shoots, respectively. The applications of the three adsorbents decreased HCB and PeCB extractability in Ac, while only the application of activated carbon decreased their extractability in An. The bioavailability of HCB and PeCB to rice plants in Ac was higher than that in An. In Ac, the applications of nano-organic SiO_2 and activated carbon decreased the BCF of HCB to rice roots by 16.1% and 26.8%, respectively, whereas only the application of activated carbon decreased the BCF of PeCB to rice roots by 31.4%, compared to the control. In An, only the application of activated carbon decreased the BCFs of HCB and PeCB to rice roots by 22.9% and 18.2%, respectively, compared to the control. However, the application of nano-organic montmorillonite inhibited rice growth in both soils. The results of this study suggested that the effectiveness of adsorbents would vary with pollutant and soil types, providing a reference point for developing efficient adsorbents to reduce the ecological risk of POPs.

Key Words: accumulation, activated carbon, bioconcentration factor, hexachlorobenzene, nano-materials, pentachlorobenzene

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INTRODUCTION

As targeted by the Stockholm Convention (2001), persistent organic pollutants (POPs) are known to remain in the environment long after application, where they are bioavailable and thus hazardous to ecological and human health (Zhang *et al.*, 2013). Most POPs can bioaccumulate in living organisms and tend to biomagnify through the food chain (UNEP, 2003). Therefore, although the production and handling of POPs are in decline worldwide, human exposure to these chemicals remains relevant to public health.

Within the families of POPs, hexachlorobenzene (HCB) and pentachlorobenzene (PeCB) are two widespread environmental pollutants, previously used in various industries (Barber *et al.*, 2005; Bailey *et al.*, 2009). The primary physco-chemical properties of HCB and PeCB were presented in Table I. Because the HCB has six chlorines on the benzene ring and the PeCB has five chlorines and one hydrogen on the benzene ring, the melting point, boiling point, and octanol/water partition coefficient ($\log K_{\mathrm{OW}}$) of HCB are higher than those of PeCB, but the vapor pressure of HCB is lower than that of PeCB. Although the commercial production of HCB and PeCB has been banned for several years in most of the world, they are still produced as industrial by-products of certain chemicals (Barber *et al.*, 2005; Bailey *et al.*, 2009). In addition, the HCB and PeCB have the potential for bioaccumulation through food chain (Sweetman *et al.*, 2005; Yang *et al.*, 2008). Therefore, the ecological risk of HCB and PeCB in the environment needs widespread attention.

The key issue of environmental effects for POPs in soils is their bioavailability. As POPs are aging in soils,

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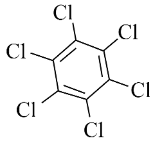
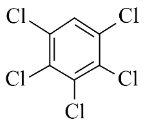
TABLE I

Physco-chemical properties of the persistent organic pollutants (POPs), hexachlorobenzene (HCB) and pentachlorobenzene (PeCB)

POP	Molecular structure	Molecular formula	Melting point	Boiling point	$\log K_{OW}$[a] (25 °C)	Vapor pressure (25 °C)
			°C	°C		kPa
HCB		C_6Cl_6	226	323	6.2	1.5×10^{-6}
PeCB		C_6HCl_5	86	276	5.0	1.0×10^{-3}

[a] Octanol/water partition coefficient.

a portion is tightly adsorbed by soil organic matter (SOM) or entrapped within soil micropores. It has been reported that only the readily water-soluble and loosely bound POPs are bioavailable (Tao *et al.*, 2004), while the tightly adsorbed fraction is considered non-bioavailable (Alexander, 2000; Song *et al.*, 2011; Liu *et al.*, 2013). As such, one possible way to reduce the bioavailability of POPs is to amend soils with adsorbent materials.

Soil amendments have been used to reduce bioavailability of a variety of pollutants through increasing adsorption or binding (Hsu *et al.*, 2000; Krishna *et al.*, 2001; Pal and Vanjara, 2001; Erdoğa *et al.*, 2008). Natural materials that mimic adsorbents in soils, such as SOM, clays, or minerals, are preferred. For example, biochar has a strong sorption affinity and has been used to reduce contaminant bioavailability (Kookana, 2010; Song *et al.*, 2012). Montmorillonite clay and silicon dioxide (SiO_2) have high surface areas and swelling properties due to their sheet structures, as well as high cation exchange capacities, making them effective in adsorbing inorganic pollutants. After processing by organic modification, they can also adsorb organic pollutants effectively (Zhu *et al.*, 2012; Yang *et al.*, 2015). Natural nano-materials have been widely applied as adsorbents in the management of waste water (Kıranşan *et al.*, 2014; Hassani *et al.*, 2015). However, to date there is limited research on the adsorption of POPs in soils by organically modified nano-materials. In addition, adding any modified materials to soil may induce unintended adverse environmental effects (Asli and Neumann, 2009; Dietz and Herth, 2011). Therefore, greenhouse tests to determine the safety and effectiveness of these materials are necessary, prior to the application of these materials in contaminated soils at the field scale.

Soils are an important reservoir for HCB and PeCB due to their high organic carbon contents (Covaci *et al.*, 2001; Meijer *et al.*, 2003; Sweetman *et al.*, 2005). Food crops, which serve as the first link in the human food chain, are susceptible to contamination by soil HCB and PeCB (Wang and Jones, 1994; Beck *et al.*, 1996; Su and Zhu, 2006). In Southeast Asian countries, rice (*Oryza sativa* L.) is a staple food, and rice straw is important as feed for livestock (Yang *et al.*, 2008); POPs could therefore enter the human food chain by consumption of contaminated rice or meat from livestock raised on contaminated straw. Thus, methods to reduce the risk of HCB and PeCB uptake by rice are essential. The primary pathway of HCB and PeCB uptake by rice plants is from soils (Yang *et al.*, 2008; Liu *et al.*, 2013). Therefore, exploring efficient adsorbents to decrease HCB and PeCB bioavailability in soils is the key to reducing the risk of rice uptake.

The objective of this study was to explore the effect of natural nano-materials with organic modification on the HCB and PeCB bioavailability to rice plants in different soils in a greenhouse experiment. Three adsorbents, nano-organic montmorillonite, nano-organic SiO_2, and activated carbon, were applied to two soils at the seedling stage of rice. The results of this study will provide a reference point for the development of methods and materials to reduce the risk of POPs in soils.

MATERIALS AND METHODS

Chemicals and reagents

Standard samples of HCB and PeCB (purity > 99.5%) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Hexane, acetone, dichloromethane, and Na_2SO_4 (analytical grade) were purchased from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). The Na_2SO_4 was oven-dried at 400 °C for 4 h.