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The effects of different types of crop straw on the transformation of pentachlorophenol in flooded paddy soil☆

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ABSTRACT

The incorporation of various types of crop straw to agricultural soils has long been practiced to improve soil fertility. However, the effects of crop straw on the fate of organo-chlorine pesticides in flooded paddy soils are not well understood. The dechlorination of pentachlorophenol (PCP) in four vertical profiles (0-10, 10-20, 20-30, 30-50 mm depth) of two flooded paddy soils, a Plinthudult (Soil 1) and a Tropudult (Soil 2) was investigated following the application of four crop straws (rice, wheat, rape and Chinese milk vetch) to them. In all treatments, PCP dechlorination decreased with increasing soil depth. In the crop straw treatments, PCP was almost completely dechlorinated within 60 days, and rapidly transformed to 2,3,4,5-tetrachlorophenol, and further to 3,4,5-trichlorophenol. Further dechlorination of 3,4,5-trichlorophenol also occurred in all treatments except for the rape straw. It is possible that the NH_4^+ and NO_3^- derived from the straw are responsible for the inhibition of the 3,4,5-trichlorophenol dechlorination. The reduction of Fe (III) and SO_4^{2-} increased following application of the crop straws. The RDA analysis indicated that the Fe (III) reducing bacteria might be involved in the ortho-dechlorination, while SO_4^{2-} reducing bacteria were involved in para- and meta-dechlorination of PCP. The complete detoxification of PCP depended upon both the crop straw type and soil properties.

1. Introduction

Pentachlorophenol (PCP), a major pollutant in China, has been used to kill *Oncomelania hupensis* which is the intermediate host of schistosomiasis (Lin et al., 2012). Although the application of PCP in agriculture has been banned for about 16 years, it is still detected in the environment due to its high stability (Chen et al., 2016a, 2016b). Soils and sediments are major pesticides sinks and are also potential sources of re-emission (Diagboya et al., 2016). Hence, the transformation of PCP in soils has been the focus of current research (Chen et al., 2016b).

Paddy soils cover a total global area of approximately 165 million ha (Long et al., 2015), which are subjected to periodic changes in redox conditions. Paddy soils switch from oxic to anoxic conditions after flooding (Li et al., 2016). Oscillations between reducing and oxidizing conditions were observed at the soil-water interface of flooded soils (Mejia et al., 2016).

PCP dechlorination in anaerobic soils has received increased attention during recent decades (Tong et al., 2015), but little is known about PCP dechlorination in the soil-water interface of flooded soils linked to the geochemical reactions of the chemical moieties they contain, especially the dechlorination mechanism(s).

Previous studies showed that PCP dechlorination is closely correlated with the geochemical cycles of C, Fe and S in soil (Xu et al., 2015; Chen et al., 2016b). The dechlorination mechanisms of PCP include ortho-, meta-, para-dechlorination and further mineralization, which require the activity of various microorganisms. Limam et al. (2016) demonstrated the dechlorination of PCP and 2,4,6-TCP into 4-CP under methanogenic conditions. The lack of corresponding dechlorination microorganisms may result in the accumulation of intermediate products in soils (Xu et al., 2015), including some toxic products. The 3-, 4- and 5- chlorine substitution increases the toxicity of chlorophenol while 3,4,5-trichlorophenol is regarded as the most toxic chlorophenol (Czaplicka, 2004). Additionally, the toxicity of chlorophenol and soil properties are closely correlated (Martí et al., 2011). Currently, there is a lack of understanding of PCP dechlorination and intermediate

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production in paddy soils.

Straw incorporation is an important practice to ensure the sustainable development of agriculture and is widely used to improve the physical and chemical properties of soil (Nicolardot et al., 2007; Pan et al., 2017). In China, there are roughly 1.7×10^8 tons of rice straw and 6.7×10^4 tons of straw carbon produced annually (Ji et al., 2012). The incorporation of crop straw may change important soil properties, which will have a great impact on the movement and transformations of pollutants in paddy soils (Alletto et al., 2008). Crop straw inputs could influence the dechlorination pathways of pesticides in soil, depending upon their varieties and chemical composition (Freixa et al., 2016). Alletto et al. (2008) found that the addition of corn and oat straw influenced the behavior of isoxaflutole in soils, including its mineralization, formation of bound residues and intermediates. However, it is still not known if the incorporation of crop straws can impact the dechlorination of PCP in paddy soils.

The dechlorination mechanism(s) of PCP have not yet been fully evaluated in paddy soil, expecially the dechlorination pathway following crop straw applicaton. The aim of this study was to investigate (i) the redox reaction in vertical profiles of flooded paddy soil (0-10, 10-20, 20-30, 30-50 mm) in response to crop straw application and (ii) the effects of crop straw on PCP dechlorination and intermediate production. The results obtained are planned to extend our knowledge of the mechanisms of PCP dechlorination in flooded paddy soil following straw incorporation.

2. Materials and methods

2.1. Soils

Two paddy soils were collected from Jiangxi and Guangdong province in China. Soil samples were taken from the surface layer (0-20 cm depth), air-dried, milled and sieved < 1 mm prior to use. The soils were classified using the USDA seventh edition of the Keys to Soil Taxonomy (Soil Survey Staff, 1996). The soil characteristics are presented in Table S1 in supplementary information (SI).

2.2. Chemicals

Pentachlorophenol (PCP, >98% purity) was obtained from Sigma-Aldrich (St. Louis, MO, USA). The 3,4,5-trichlorophenol (3,4,5-TCP) and 2,3,4,5-tetrachlorophenol (2,3,4,5-TeCP) were obtained from J&K Scientific Ltd. (Beijing, China). Methanol (>99.9% purity) was obtained from Merck KGaAb (Darmstadt, Germany). The other analytical grade chemicals were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China).

2.3. Crop straw

The four, field grown, crop straws were: rice (*Oryza sativa* L.), wheat (*Triticum aestivum* L.), rape (*Brassica rapa* subsp. *oleifera*) and Chinese milk vetch (*Astragalus sinicus* L.). The straws were oven-dried at 65 °C for 24 h, and chopped with scissors to an average size of 2 mm prior to use.

2.4. Experiment design

The PCP polluted soils were prepared by previously described methods (Lin et al., 2012). In brief, to prepare xenobiotic spiked soil, PCP solution (1000 mg L^{-1}) in methanol was mixed with a portion of soil. The spiked soil was vented for 24 h to allow the methanol to vaporize and then mixed thoroughly with a large portion of uncontaminated soil (1:19, w/w). Then, the straws were homogeneously mixed with soils previously amended with 50 mg PCP kg^{-1} soil. The amended soils were transferred to 250 mL beakers to provide 7 cm thick soil layers and incubated for 14 days at room temperature. Then, Milli-Q water was added to form a 2 cm water layer covering the soil surfaces. The greenhouse temperatures were 30–35 °C during daytime and 25–30 °C at night. Water lost by evaporation was replenished with Milli-Q water daily. Soils were sampled at 30, 60 and 120 days incubation by sacrificing individual replicates. The sampling procedure was as follows: firstly, 4 days before sampling, the surface water was allowed to evaporate without replenishment; secondly, 0-10 mm, 10-20 mm, 20-30 mm, 30-50 mm layer soils were collected using a modified 20 mL syringe; thirdly, Cl^-, SO_4^{2-}, NH_4^+, HCl-extractable Fe (III) and Fe (II), dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) in fresh soils were analysed immediately. PCP concentrations in soils were analysed after freeze-drying. Three replicates were used in each treatment.

2.5. Analytical methods

Soil properties, straw propeties (including C, N, S, DOC, NO_3^- and NH_4^+), and inorganic ions (Fe(III), Fe(II), SO_4^{2-}, NH_4^+, and Cl^-) in soil samples were analysed following previously described methods (Lin et al., 2012, 2014; Ratering and Schnell, 2000). Details can be found in supplementary information (SI).

The microbial community structure was determined by phospholipid fatty acid (PLFA) analysis. The method was based on that described by Wu et al. (2012). Details can be found in SI. The monounsaturated PLFAs (14:1ω5c, 15:1ω6c, 16:1ω5c, 16:1ω7c, 16:1ω9c, 17:1ω8c, 18:1ω7c, 18:1ω9c, 20:1ω9c) and branched PLFAs (i13:0, i14:0, i15:0, a15:0, i16:0, a16:0, i17:0, a17:0, 10me 16:0, 10me 17:0, 12:0 2OH, 15:0 3OH, 16:1 2OH) were used as indicators of aerobic and anaerobic microbial communities respectively (Yang et al., 2016). The 16:0 10 Me was used to indicate sulphate reducing bacteria (Xu et al., 2015). The Fe (III) reducing bacteria were indicated by the 16:1ω7c (the major PLFA in *Geobacter metallireducens* and *Shewanella sp.*, which are well known as iron-reducing bacteria) (Xu et al., 2015).

The concentrations of PCP and intermediate products (2,3,4,5-TeCP and 3,4,5-TCP) in soils were determined by ultrasonic extraction and HPLC analysis (Chen et al., 2012; Lin et al., 2014). In brief, 2 g soil was adjusted to pH 4 with 130 μl 9 mol L^{-1} H_2SO_4 and then extracted in 10 mL methanol by ultrasonics (60 kHz, 25 °C) for 30 min. After centrifugation at 1680*g* for 10 min, the supernatants were collected. The soils were then extracted twice more as described above. The supernatants were combined and concentrated to 1 mL in a rotary evaporator. Finally, each sample was filtered through a 0.22 μm Millipore membrane (ANPEL, 13 mm diameter) prior to analysis. Details of the HPLC analysis can be found in supplementary information (SI). The average recovery of PCP, 2,3,4,5-TeCP and 3,4,5-TCP were 96.05 ± 3.21%, 96.40 ± 5.01% and 98.23 ± 3.81% respectively. The method detection limits of PCP, 2,3,4,5-TeCP and 3,4,5-TCP were 0.01, 0.01, 0.02 mg kg^{-1}, respectively.

The intermediate products of PCP (2,3,4,5-TeCP and 3,4,5-TCP) were identified using an Agilent 1100 high performance liquid chromatograph (Agilent Technologies, Palo Alto, CA, USA) coupled with a quadrupole MS system equipped with ESI source (Chung et al., 2013; Lin et al., 2017). A C18 column (5 μm, 4.6 × 250 mm) was chosen to separate intermediate products. The conditions were: 30 °C column temperature; 20 μl injection volume; 10:90 v/v of 1% acetic acid: methanol elution; 1 mL min^{-1} flow; 300 °C ionization temperature; +4.0 kV and −3.5 kV ESI voltage for positive and negative modes; 100-600 m/z scan range at 1.0 s/scan. The intermediate products of PCP were further identified by GC-MS (Chen et al., 2012; Xu et al., 2015). The extraction of