Spatial and temporal variations in pentachlorophenol dissipation at the aerobic–anaerobic interfaces of flooded paddy soils

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ABSTRACT

Pentachlorophenol (PCP) dissipation occurs naturally in flooded soils and although dissipation half-lives vary between soil profiles at the millimeter-scale the reason is poorly understood. Vertical variations of PCP dissipation were investigated in three typical Chinese paddy soils; Soil 1 (Umbraqualf), Soil 2 (Plinthudult) and Soil 3 (Tropudult). The soil depth was divided into a surface and a deep layer based upon different PCP dissipations in the surface layer of 40–93, 42–88 and 16–100% for Soils 1–3 respectively. In the deep layer, PCP was greatly dissipated in Soil 2, but much less in Soil 1 and Soil 3. Correlation analysis indicated that SO_4^{2-} and Fe(III) were negatively related to PCP dissipation. SO_4^{2-} and Cl$^-$ were highly mobile in the flooded soil profiles. Fe(III) reduction increased with increasing soil depth, and was inhibited by high SO_4^{2-} concentrations.

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1. Introduction

Paddy soils are subjected to periodic changes in redox conditions (Ratering and Schnell, 2001). The flooded water and its surrounding environment support a variety of physical, chemical, and biological processes in the soil profiles (Usui and Kasubuchi, 2011). The depth of this active soil layer is usually modeled as 1–5 cm (Luo et al., 2012). Ratering and Schnell (2000) reported that depth profiles of Fe(II) and Fe(III), SO_4^{2-} and NO_3^- concentrations have shown that the redox reaction is intense in the 0–10 mm depth soil surface layer after flooding. The Fe(III) profiles of flooded paddy soils indicated oxidation of Fe(II) in the upper 6 mm soil layer (Ratering and Schnell, 2001). There was also high oxygen availability in the upper 3 mm during a 7-week under light (Ratering and Schnell, 2001). In contrast, when incubated in the dark, within 6 h of flooding, oxygen was depleted below 0.2 mm at the floodwater–soil interface to undetectable concentrations at a depth of approximately 2 mm (Noll et al., 2005). Weber et al. (2006) reported that the significance of phototrophic Fe(II) oxidation in natural terrestrial environments was limited by the maximum penetration of light to 0.2 mm in soil and sediment. Below this depth, NO_3^- could be used as an electron acceptor instead of oxygen for the oxidation of Fe(II), while NO_3^- was generated by nitrification from ammonium, which increased *n* with soil depth (Ratering and Schnell, 2001).

Previous studies showed that many biogeochemical processes are accelerated due to changes in physical, chemical and biological conditions in soil profiles caused by the prevalence of the adjacent aerobic and anaerobic zones (Reddy et al., 1989; Meade and D'Angelo, 2005). However, many studies have focused on biocide dissipation, water transport and ion mobilization in unsaturated soil profiles (Cahill and Parlange, 1998; Parlange et al., 1998; Alletto et al., 2006). The fate of biocides was shown to be strongly dependent on organic matter content in soil surface layers but more dependent on clay content in subsurface ones (Alletto et al., 2006; Ghafoor et al., 2011). The soil surface layer is rich in organic matter which increases sorption reactions and microbial activity. However, in the subsurface layer, the organic matter is limited and clay dominates biocide sorption and abiotic degradation (Alletto et al., 2006; Rodriguez-Cruz et al., 2006). A range of environmental factors such as oxygen and temperature, which affect microbial growth rates and pesticide degradation, also change with increasing soil depth (Bending and Rodriguez-Cruz, 2007). Additionally, many studies have investigated the distribution of biocides in soils and sediments profiles of known ages *in situ* to obtain a chronological overview of contamination with respect to persistent organic pollutants (Wang et al., 2006; Gotz et al., 2007).

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Pentachlorophenol (PCP) is one of the most frequently detected pesticide contaminants in agricultural soils. It is relatively persistent, where it undergoes slow natural dissipation, by e.g. adsorption, volatilization, leaching and biodegradation (He et al., 2007; Chen et al., 2012; Puglisi et al., 2009). The main process leading to the dissipation of pesticide residues in soil is biological degradation, caused by the activities of soil microorganisms (Rodriguez-Cruz et al., 2006; Vryzas et al., 2012). The rate of biodegradation is influenced by soil chemical properties such as organic matter content, pH and nutrient status, and is also influenced by environmental conditions that control soil temperature and soil moisture (Walker et al., 2001). The dissipation of PCP is also negatively related to reduction of NO_3^-, SO_4^{2-} and Fe(III) in the aerobic–anaerobic interfaces established by the rhizosphere of rice (Hayat et al., 2011). In addition, the biodegradation of PCP under h aerobic and anaerobic conditions has been documented, and there are extensive reports of the isolation of PCP-degrading microbial strains and their metabolic degradation processes (McAllister et al., 1996; Copley et al., 2012; Hlouchova et al., 2012). However, most research has focused on the centimeter-scale or meter-scale in sediments or upland soils. How and why the dissipation half-lives of PCP varies between paddy soil profiles at the millimeter-scale under aerobic and anaerobic conditions remain unclear and require further study. In particular, the dissipation pathways and their relationships with electron acceptors are poorly understood.

Our main aims were to: (1) determine PCP dissipation in soil profiles and (2) determine how its dissipation was influenced by transformation of soil ions. Our hypothesis was that the reductive dechlorination processes of PCP dissipation in soil are significantly related to different major electron donors/acceptors.

2. Materials and methods

2.1. Soils

Three paddy soils were collected from the surface layer (0–20 cm depth) from three provinces in China, representing typical Chinese paddy soils and classified according to the USDA (Soil Survey Staff, 1996) system (Table 1). They were air-dried, ground and sieved <1 mm prior to use.

2.2. Methods

2.2.1. Analytical methods

Soil properties, (including SO_4^{2-}, Cl^-, NH_4^+, Fe(III), Fe(II) and PCP) were analyzed following previously described methods (He et al., 2009; Wu et al., 2009; Hayat et al., 2011). Details can be found in Supplementary information (SI).

All chemicals were analytical grade or above. Pentachlorophenol (>98% purity) was purchased from Aldrich Chemical Co.

2.2.2. Experimental design

To prepare xenobiotic spiked soil, 500 mL methanol containing 10 mg mL^{-1} PCP was mixed with 5 kg soil (air dry). The spiked soil was vented for 24 h to permit t methanol vaporization, then mixed thoroughly with 95 kg uncontaminated soil (1:19, w/w). A rhizobox was used to simulate water–soil interfaces, with dimensions of 230 × 230 × 230 mm (length × width × height) (Fig. 1). The soil in the rhizobox was separated into 16 sub-layers (1.2, 2.4, 3.6, 4.8, 6.0, 7.2, 8.4, 9.6, 15, 20, 25, 30, 35, 40, 45, 50 mm from the soil surface) using hollow rectangular plates (1.2 mm, thickness) made from expoxy resin with inner sizes of 200 × 150 mm. Each rhizobox was filled with 2.5 kg air-dried soil mixed thoroughly with PCP, to provide initial concentrations of 50 mg PCP kg^{-1} soil. The control treatment was prepared similarly,

but without PCP addition. After equilibration in a greenhouse for 7 days, Milli-Q water was added to create a 2 mm thick water layer covering the soil surface. Water loss was replenished with Milli-Q water every two days. The daytime temperature was 30–35 °C, the nighttime temperature was 25 °C and 30 °C.

Soils were sampled at 7, 15, 30, 60 and 120 days of incubation by sacrificing individual replicates. Firstly, 4 days before sampling, flooded water above the soil surface in three duplicate rhizoboxes was allowed to evaporate to almost reach soil saturation. Secondly, soil samples in different layers were taken using a scraper with a 1 mm beveled edge. Thirdly, fresh soils were used for all the measurement except PCP analysis, which was freeze dried prior to extraction. All operations were performed in an anaerobic glove box filled with 100% N_2.

2.2.3. Data analysis

The half-life of PCP was used to define the dissipation rate of PCP. The half-life ($t_{1/2}$) was calculated from: $t_{1/2} = T \ln 2/\ln (C_0/C_t)$, where C_0 is the initial amount of PCP, T is the incubation time, and C_t is the final amount of PCP. Pearson correlation analysis was performed to interpret the relationship between PCP dissipation (PCP$_a$) and electron donors and acceptors in soils. PCP$_a = (C_3 - C_t) * 100/C_3$, where C_t is the PCP concentration at day t (15, 30, 60, 120 days), C_3 is the PCP concentration at day 3. Correlation analysis was performed using SPSS 16.0 for windows. All values are the means of triplicate determinations.

3. Results

3.1. PCP dissipation in soil profiles

The dissipation half-lives of PCP are shown in Fig. 2. The main trend was that the half-lives of PCP increased with increasing soil depth, and reached relatively constant values in Soils 1 and 2 at about 20 cm but maintained a slow decline in Soil 3, until the maximum, 50 mm, depth. The half-lives of PCP in Soil 3 were therefore clearly different from Soils 1 and 2. The residue of PCP in soil profiles was also used to further define the dissipation.

The residual PCP during the whole incubation also showed the same trend (Fig. 3). PCP dissipation with depth in Soils 1 and 2 was less than in Soil 3 after 3 days incubation (Fig. 3). PCP in Soil 3 was more readily transferred to lower horizons during flooding than in Soil 1 and Soil 2. In Soil 1 and Soil 2, PCP was dissipated significantly ($p < 0.05$) in the 0–3.6 mm depth during the 3 day incubation (Fig. 3), while in Soil 3, significant dissipation ($p < 0.05$) occurred up to 15 mm.

The soil depth could be divided into two profiles based upon the residue and the dissipation half-lives of PCP (i.e. surface and deep layer) (Figs. 2 and 3). The surface layer clearly differed between the three soils, being 0–15 mm, 0–25 mm and 0–30 mm for Soil 1, Soil 2 and Soil 3 respectively. The PCP dissipation decreased with increasing soil depth in the surface layer, and then became similar between soil profiles in the deep layer (Fig. 3). In Soil 1, only 9% of PCP was dissipated from day 30 to 120 in the 15 to 50 mm depth (Fig. 3). In the deep layer of Soil 2, approximately 40% of PCP was dissipated at the end of the incubation. In Soil 3, the PCP concentration remained almost constant throughout in the deep layer.

3.2. Transport of Cl^- and SO_4^{2-} in soil profiles

Variations in SO_4^{2-} and Cl^- concentrations in the soil profiles are shown in Figs. 4 and 5. Concentrations changes varied widely between soils and profiles. The general trend was that initial

Table 1
Soil properties.

Soil no.	Soil type		Textural class	pH	OM (g kg^{-1})	Fe^a (g kg^{-1})	Fe$_{HCl}$ (g kg^{-1})	NO_3^- (mg kg^{-1})	SO_4^{2-} (mg kg^{-1})	Particle size (%)		
	Chinese classification	USDA classification	USDA							Clay	Silt	Sand
1	Yellow mottled soil	Umbraqualfs	Silt clay	6.0	31.3	6.1	11.2	164.8	65.16	22.2	53.1	24.7
2	Red soil	Plinthudult	Silty clay	5.4	19.6	3.8	6.5	15.6	28.6	29.1	39.7	31.2
3	Latosols	Tropudult	Clay	6.6	7.6	2.3	5.5	9.3	352.5	15.2	36.7	48.1

Fe^a, amorphous Fe_2O_3; Fe$_{HCl}$, HCl-extractable Fe_2O_3; OM, organic matter.