Reductive transformation of pentachlorophenol on the interface of subtropical soil colloids and water

Fangbai Li a,⁎, Xugang Wang c, Chengshuai Liu a, Yongtao Li b, Fang Zeng a, Liang Liu a

Abstract

Ten soil colloids were obtained from three kinds of Fe-rich (<50 g kg−1) subtropical soil parent materials (Basalt, Sandshale, and Quaternary Period Red Earth) collected in nine sites in Guangdong of China. Effect of the Fe-rich soil colloids and adding Fe(II) and oxalic acid on reductive dechlorination transformation of pentachlorophenol (PCP) were studied on colloids interfaces of reaction suspension. Mineralogical properties and specific surface area of the soil colloids were characterized by X-ray powder diffraction and Brunauer–Emmett–Teller (BET) methods, respectively. A series of reductive experiments were designed to determine PCP transformation and chloride ion release, and to calculate rate constant (k values) of pseudo first-order kinetics. Our results showed that reductive transformation of PCP occurred with k values from 0.007 to 0.057 d−1, and relevant chloride was released in the suspension of the ten soil colloids. Soil colloid developed from Basalt presented higher transformation rates (0.040–0.057 d−1) than that from Sandshale (0.007–0.033 d−1) and Quaternary Period red earth (0.012 d−1). Two paddy soil colloids developed from Sandshale (0.032–0.033 d−1) were more active than other three Sandshale soil colloids (0.007–0.011 d−1). The k values were significantly and positively correlated to the BET surface area (P=0.01, n=10). Addition of oxalic acid (0.022–0.231 d−1) or Fe(II) (0.029–0.256 d−1) into suspension of soil colloids gave rise to increase by 1.2–9.4 times in the k values. The release of chloride ion was simultaneously elevated. The enhancement of oxalic acid or Fe(II) on reductive transformation of PCP was attributed to increase of surface-bound Fe(II), which possess high reductive reactivity. The k values adding 1.0 mM oxalic acid were significantly and positively correlated to BET surface area and soil pH (P<0.01), while k values adding 1.0 mM Fe(II) were related to total Fe (P<0.001). The results may give new insight to understand the contribution of PCP abiotic reductive transformation in subtropical and tropical soils, and also in permeable reactive barriers.

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1. Introduction

Excessive application of fertilizers and pesticides caused serious organic contamination in subtropical China (Zhu et al., 2007; Chen, 2007; Li et al., 2007). Pentachlorophenol (PCP, C6Cl5OH) is extensively used as important component of fungicides, bactericides, herbicides, insecticides, molluscides, biocides, and wood preservatives in subtropical region (Crosby et al., 1981; Zheng et al., 2000; Hong et al., 2005). However, PCP is also a kind of ionizable hydrophobic organic contaminants with acute toxicity, persistent to biodegradation and chemical stability. It has been reported that adverse effects of PCP on environment and human being might last for a long time (He et al., 2005; Tamer et al., 2006). PCP has been designated as a priority pollutant and a probable human carcinogen (Keith and Tellier, 1979). Therefore, the degradation and transformation of PCP in soil is greatly concerned.

The degradation and transformation of PCP could be driven by chemicals and microorganisms (Vogel et al., 1987; Smidt and de Vos, 2004; Henderson and Demond, 2007). For examples, manganese oxides can drive the oxidative degradation of PCP (Petrie et al., 2002; Zhao et al., 2006). Furthermore, the abiotic adsorption and degradation of PCP on the surface of minerals and materials have received much attention in the past decades. These minerals and materials for PCP removal included organoclay (Stapleton et al., 1994), carbonized bark (Edgehill and Lu, 1998), peat-bentonite mixtures (Viraraghavan and Slough, 1999), granular activated carbon (Leyva Ramos et al., 2003; Diaz-Flores et al., 2006), iron oxides (Lee and Batchelor, 2002a,b), and chitosan (Zheng et al., 2004). However, the oxidative degradation in contaminated soil is often limited when soil contains low concentrations of oxygen. Generally, the reductive transformation of polychlorinated organic compounds should be a critical degradation way in anoxic condition. In particular, microbial reductive dechlorination transformation of polychlorinated organic compounds has been received great attention as an efficient way for a long time (Vogel et al., 1987; Smidt and de Vos, 2004; Yoshida et al., 2007).
However, the abiotic reductive dechlorination transformation processes have to be considered in the presence of some synthesized or natural reductants in environments. Sulfide compounds in landfill leachate and estuary sediments were reported to act as an electron donor in reductive dechlorination (Kriegman-King and Reinhard, 1992; Cruritis and Reinhard, 1994; Kriegman-King, 1994), iron-bearing soil minerals that are abundant in soil environment were also used as reductants. Iron-bearing minerals (Butler and Hayes, 1998; Butler and Hayes, 1999; Lee and Batchelor, 2002a, b, 2004) and zero valent iron reductants. Iron-bearing minerals (Butler and Hayes, 1998; Butler and Hayes, 1999; Lee and Batchelor, 2002a, b, 2004) and zero valent iron reductants. Iron-bearing minerals (Butler and Hayes, 1998; Butler and Hayes, 1999; Lee and Batchelor, 2002a, b, 2004) and zero valent iron reductants. Iron-bearing minerals (Butler and Hayes, 1998; Butler and Hayes, 1999; Lee and Batchelor, 2002a, b, 2004) and zero valent iron reductants. In soil environment, structural Fe(II) as iron oxides, iron sulfoles, and green rusts, and adsorbed Fe(II) species are important natural reductants. Iron contents are considerably high in tropical and subtropical soils (Schoonen et al., 1998). In these soil profiles, a large amount of Fe-minerals occur as free ammonous or crystal iron (hydro) oxides with high geochemical activity. The dominant soil types in tropical and partly tropical Guangdong province, China, including Rhodic Hapli–Udic Ferrosol, Plinthic Hapli–Udic Ferrosol and Typic Hapli–Udic Ferrosol, contain more than 2% iron (Liu, 1993). The occurrence of structural and amorphous-Fe(II) species in the soil provides a possible condition of abiotic reductive transformation of polychlorinated organic compounds. Consequently, our objective was to study the effect of Fe-rich soil colloids from different parent materials on pentachlorophenol reductive transformations on the interface of soil colloids and water.

2. Materials and methods

2.1. Soil colloids

Ten cultivated surface soils (0–15 cm) were collected from different sites in subtropical Guangdong province, China. The soil classification and their abbreviated name were described in Table 1. Within each sampling unit, soils were taken from several different locations (5–10 locations, depending on the uniformity and size of the sampling unit), and mixed into one composite sample. The soil colloids were obtained by the following procedure: firstly, the collected soils were ground to pass a 100 mesh sieve (with diameter <35 μm), secondly, to be dispersed by adding 0.01 M NaOH solution dropwise while placed in the ultrasonator. Then, the soil sample (2–12 μl) was separated by precipitation; At last, the precipitations were dried at 55 °C for 60 h to obtain the soil colloids. The soil colloids were ground to pass through 100 mesh sieve prior to use.

2.2. Analysis of chemical properties of soil colloids

Soil pH was measured with a Leci pHs-3C pH meter after extraction in water (1:5) by shaking for 1 h. Organic matter contents of the soil colloids were determined by the modified Tjurin dichromate method using wet combustion with external heating at 160 °C for 0.5 h (Nikitin, 1999). Total iron in the soil colloids were digested with nitric acid (Guaranteed Reagent), perchloric acid (Guaranteed Reagent), and hydrofluoric acid (Guaranteed Reagent). DCB-Fe was extracted by dithionite-citrate-bicarbonate (DCB) method, amorphous-Fe was extracted by acidified ammonium oxalate buffer solution at pH 3.0, while complexed-Fe was extracted by alkali sodium pyrophosphate at pH 8.5 (Agbenin and Olojo, 2004; Pansu and Gautheyrou, 2006). The Fe concentration in the extracting solution was determined by 1,10-phenanthroline method (Fadrus and Malý, 1975). This technique involves the complexation of Fe(II) with 1,10-phenanthroline in a sodium acetate buffer, and a UV–Vis spectrophotometer (UV–Vis TU-1800, Purkinje General, Beijing) was used to determine absorbance at a wavelength of 510 nm.

2.3. Determination of mineralogical and physical properties of soil colloids

The X-ray powder diffraction (XRD) patterns of the soil colloids were characterized with a Rigaku D/Max-III A diffract meter. The operation was performed at ambient temperature, 30 kV and 30 mA, and a Cu Kα radiation (λ=0.15418 nm). The composing phases were identified through comparing diffraction patterns with those on the standard...
77 K was applied and Carlo Erba Sorptometer was used (Yu et al., 2003).

2.4. Chemicals used in the experiments

Grade. Deaerated Milli-Q water (DMW), prepared by deoxygenating with Milli-Q system. Organic solvents used were either HPLC or analytical grade. All solutions were prepared with high purity water obtained from a Milli-Q system. Oxalic acid (analytical grade) was purchased from Fluka. Other chemicals of analytical grade were purchased from Guangzhou Chemical Co., China. Stock solutions of 0.25 M oxalic acid was prepared in the chamber, and then preserved in a dark-brown container. All stock solutions were filtered through 0.2 μm filters before used.

2.5. Abiotic transformation reactors and procedure

Unless otherwise stated, all experiments were carried out in an anaerobic chamber (99.999% N₂ at a flow rate of 80 mL min⁻¹) in triplicate. The reactors were composed of 20 mL borosilicate glass serum bottles with aluminum crimps and Teflon-lined butyl rubber septa, and put in an orbital shaker at 200 rpm and incubated at 25±1 °C in the dark during the reaction process. In order to avoid microbial interaction during the dechlorination process, before reaction process, all the soil colloids were soaked with 95% ethanol and spread in a thin even layer under 253.7 nm UV radiation (germicidal) in a sterile hood for about 4 h for sterilization.

During the reaction process, 10 g L⁻¹ soil colloid and 20 mL of 0.038 mM deoxygenated PCP solutions were added into the borosilicate glass serum bottles. After deoxygenation for 2 h with purged N₂, the bottles were sealed and airproofed. Then the bottles were purged N₂ for 2 h, was used to prepare the aqueous solutions. The stock solution of 0.038 mM PCP was prepared by dissolving 10 mg PCP in 10 mL absolute ethyl alcohol and then adjusting the volume to 1 L using DMW purged with O₂-free N₂ overnight. Aqueous solutions of Fe(II) were prepared from ferrous ammonium sulfate. Fresh stock solutions of ferrous ion (0.25 M) were prepared prior to each experiment in an anaerobic chamber containing high purity N₂ headspace, and stored in dark-brown glass bottles that were wrapped with aluminum foil to exclude light. Fe(II) solution was calibrated by titrating against primary standard K₂Cr₂O₇ by using the 1,10-phenanthroline method (Jeon et al., 2003). Stock solution of 0.25 M oxalic acid was prepared in the chamber, and then preserved in a dark-brown container. All stock solutions were filtered through 0.2 μm filters before used.

2.6. Aqueous phase mineral analysis

Powder XRD cards compiled by the Joint Committee on Powder Diffraction Standards (JCPDS, 1979). The BET surface area was measured by the Brunauer–Emmett–Teller (BET) method. The N₂ desorption at 77 K was applied and Carlo Erba Sorptometer was used (Yu et al., 2003).

Pentachlorophenol (PCP ~99%) was purchased from Aldrich. Oxalic acid (analytical grade) was purchased from Fluka. Other chemicals of analytical grade were purchased from Guangzhou Chemical Co., China. All solutions were prepared with high purity water obtained from a Milli-Q system. Organic solvents used were either HPLC or analytical grade. Deaerated Milli-Q water (DMW), prepared by deoxygenating with 99.999% nitrogen for 2 h, was used to prepare the aqueous solutions. The stock solution of 0.038 mM PCP was prepared by dissolving 10 mg PCP in 10 mL absolute ethyl alcohol and then adjusting the volume to 1 L using DMW purged with O₂-free N₂ overnight. Aqueous solutions of Fe(II) were prepared from ferrous ammonium sulfate. Fresh stock solutions of ferrous ion (0.25 M) were prepared prior to each experiment in an anaerobic chamber containing high purity N₂ headspace, and stored in dark-brown glass bottles that were wrapped with aluminum foil to exclude light. Fe(II) solution was calibrated by titrating against primary standard K₂Cr₂O₇ by using the 1,10-phenanthroline method (Jeon et al., 2003). Stock solution of 0.25 M oxalic acid was prepared in the chamber, and then preserved in a dark-brown container. All stock solutions were filtered through 0.2 μm filters before used.

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with reaction suspension were placed in the anaerobic chamber, shaking at 200 rpm with the constant temperature of 25±1 °C. At the given time intervals, one of the bottles were taken out for needed analysis as shown in followed Section 2.6.

To investigate the effects of oxalic acid or ferrous ions on the abiotic transformation of PCP, 1.0 mM of stock solution of oxalic acid or ferrous ion was added into the soil colloid suspension. In this paper, the treatment of PCP transformation with soil colloids only was labeled as T1 (soil colloid), that with soil colloids and added oxalic acid was labeled as T2 (soil colloid+oxalic acid), and that with soil colloids and added Fe(II) was labeled as T3 (soil colloid+Fe(II)). Controls were prepared in a similar manner without adding soil colloid.

The PCP transformation was analyzed by pseudo first-order kinetics equation: \( \frac{dC}{dt} = -kt \), where \( C \) is the average concentration of triplicate PCP (mM), \( t \) is reaction time (d), and \( k \) is first-order rate constant (d\(^{-1}\)).

### 2.6. Analytical procedure of PCP transformation

At each sample intervals, one of the 20 mL serum bottle was removed to anaerobic chamber. After mixed, 1.0 mL×4 of the suspension was

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**Fig. 2.** PCP Transformation on the surface of the ten soil colloids. (T1 refers to transformation of pentachlorophenol on the surface of soil colloids only, transformation in presence of 1.0 mM oxalic acid and 1.0 mM Fe(II) is line T2 and T3, respectively; and the Control refers to PCP transformation without any soil colloids).
serum bottles to determine Fe(II) concentration, and the rest was immediately centrifuged at 4000 rpm for 10 min to remove the particles for further analysis. The supernates were stored in refrigerator at 4 °C and analyzed as soon as possible in 12 h.

PCP analysis was performed by high performance liquid chromatography (HPLC), which was consisted of a Waters 1525 Binary pump and a Waters 2487 dual λ Absorbance UV/Vis detector at 295 nm. The limit of PCP analysis in HPLC here is at 1.1×10^{-4} mM. All separations were achieved on an analytical reversed phase column (5 μm Symmetry-C18, 4.6 mm i.d. × 25 cm long, Waters, USA) and the mobile phase was 80:20 methanol/water at a flow rate of 1.0 mL min^{-1} under isocratic conditions at room temperature. The Breeze software was used. The relative standard deviation for HPLC analysis was controlled within 5%.

To analyze the intermediates during PCP reductive transformation, 20 mL supernate was acidified by the addition of hydrochloric acid to pH=2. Then, sodium chloride was added until saturation. After that, 15 mL ethyl ether was added to extract PCP. The vial was then placed on the shaker table for 10 min. Intermediates analyses were accomplished with a GC2010 gas chromatography (GC) equipped with a QP2010 plus mass selective detector (MSD) and a capillary column (RTX-1MS, 30 m×0.25 mm×0.25 μm) (SHIMADZU, Japan). Splitless mode injection of 2 μL of sample and a solvent delayed at 4.5 min were used. The injection port and ion source temperature were maintained at 250 and 200 °C, respectively. The column temperature was initially set at 55 °C for 2 min, raised to 200 °C at the speed of 20 °C min^{-1}, then raised to 250 °C at the speed of 10 °C min^{-1}, and then held at 250 °C for 5 min. The helium carrier gas flow rate was at 1.0 mL min^{-1}. Mass spectra were acquired at the electron ionization mode (EI) with an electron multiplier voltage of 1000 eV. The mass scanning ranged between m/z 50 and 300.

Determination of dissolved Fe(II), total Fe(II) and surface-bound Fe(II) species during PCP reductive transformation was reported by our group (Li et al., 2008). Dissolved Fe(II) in the solution was analyzed by the 1,10-phenanthroline method as described above. Concentrations of 0.5 M HCl-extractable Fe(II) in the serum bottles were measured by withdrawing 1.0 mL of the suspensions using N2-purged syringes, and then the aliquots were extracted by 4.0 mL of 0.5 M HCl at 25±1 °C in the dark for about 20 h (Jeon et al., 2003). After filtrated through a 0.2 μm syringe filter, the 0.5 M HCl-extractable Fe(II) was also analyzed using the 1,10-phenanthroline method. The surface-bound Fe(II) was calculated from the difference between 0.5 M HCl-extractable Fe(II) and dissolved Fe(II).

3. Results

3.1. Properties of the soil colloids

Some basic physicochemical properties of the ten soil colloids were presented in Table 2. The pH of colloids was acidic ranging from 4.09 to 6.35. Total organic carbon (TOC) contents varied considerably with maximum 84.0 g kg^{-1} in Q-TF and minimum 6.8 g kg^{-1} in B-TFA. The ten soil colloids exhibited high Fe contents with more than 50 g kg^{-1}. The main Fe fractions were DCB-Fe, which accounted for more than 60% of total Fe, except for Q-TF (48.3%). Complexed-Fe contents were the lowest among all Fe fractions, which were lower than 0.129% of total Fe.

The clay mineralogy of the soil colloids (Fig. 1) showed that the soil colloids derived from same parent material had similar mineral composition. The predominant clay minerals in four soil colloids from Basalt, i.e. B-TFA, B-RF, B-PF, and B-XF, were kaolinite, quartz, gibbsite,
and two iron oxides. Hematite and goethite were also found in these soil colloids. The predominant clay minerals in S-PF, S-RF and S-TF from Sandshale were lizardite, nacrite, dickite and kaolinite. The four clay minerals in the soil colloid from Sandshale were also found in Q-TF. However, other two clay minerals, gibbsite and illites, were also found in this soil colloid. For S-TFA and S-TGA derived from paddy, halloysite was the main clay mineral.

The BET surface areas (Table 2) of the ten soil colloids ranged from 31.8 to 72.5 m² g⁻¹. The B-XF developed from Basalt had the highest BET surface area of 72.5 m² g⁻¹, while the Q-TF developed from Quaternary Period red earth had the lowest BET surface area of 31.8 m² g⁻¹.  

3.2. Transformation of PCP in the soil colloids

The PCP transformation can be well described by pseudo first-order kinetics, and the rate constant (k) and their significance level for kinetic analysis (n=8) for PCP transformation in different soil colloids were listed in Table 3. The results of PCP transformation on the surface of the ten soil colloids under different conditions (Fig. 2) showed that the transformation was almost negligible in solution of control (without colloids). As comparison, PCP was obviously transformed in T1 treatment (exposed to soil colloids alone). The constants k value of PCP transformation rate in T1 treatments was 0.032±0.002, 0.057±0.003, 0.040±0.003, 0.019±0.002, 0.007±0.001, 0.011±0.001, 0.011±0.001, 0.032±0.004, 0.033±0.003 and 0.012±0.001 d⁻¹ within 19 d in the presence of soil colloids derived from B-RF, B-PF, B-XF, B-TFA, S-RF, S-PF, S-TF, S-TFA, S-TGA and Q-TF, respectively. Transformation rate on the surface of soil colloids derived from Basalt soil were relatively high. Especially, the rate constant of PCP transformation by B-PF was 0.057±0.003 d⁻¹, which was the highest constant among all the soil colloids. The rate constants for PCP transformation on soil colloids derived from Sandshale soils and Quaternary Period red soil were relatively low. Two paddy soil colloids developed from Sandshale (0.032±0.004, 0.033±0.003 d⁻¹) were more active than other three Sandshale soil colloids (0.007±0.001−0.011±0.001 d⁻¹). These results indicate that PCP transformation on the surface of the soil colloids should depend on soil parent materials.

The effects of adding 1.0 mM oxalic acid on PCP transformation (T2 treatment) were studied in the reaction suspension. The result showed oxalic acid enhanced the rate of PCP transformation on the surface of colloids (Fig. 2). The constant k values of PCP transformation rate in T2 treatments increased to 0.043±0.018, 0.155±0.015, 0.186±0.018, 0.092±0.010, 0.053±0.005, 0.022±0.002, 0.033±0.001, 0.086±0.007, 0.231±0.029 and 0.047±0.005 d⁻¹ on the soil colloids derived from B-RF, B-PF, B-XF, B-TFA, S-RF, S-PF, S-TF, S-TFA, S-TGA and Q-TF, respectively. The k values of T2 treatments increased by 1.3, 2.7, 4.7, 4.8, 5.5, 9.4, 5.5, 2.6, 1.3, 1.1 and 4.3 times than T1 (with soil colloids alone), respectively.

The effects of 1.0 mM Fe(II) on the transformation were also determined as T3 treatments (Fig. 2). Our results showed that the presence of 1.0 mM ferrous promoted the PCP transformation. Compared to T1 treatment, the k values increased up to 0.256±0.022, 0.150±0.011, 0.100±0.010, 0.104±0.017, 0.066±0.004, 0.060±0.006, 0.029±0.002, 0.036±0.007, 0.043±0.001 and 0.051±0.006 d⁻¹ on the soil colloids derived from B-RF, B-PF, B-XF, B-TFA, S-RF, S-PF, S-TF, S-TFA, S-TGA, S-TGA and Q-TF, respectively. The k values of T3 treatments increased by 1.3, 2.0, 4.1, 4.4, 6.5, 9.5, 5.5, 2.6, 1.3, 1.1 and 4.3 times than T1 (with soil colloids alone), respectively.

3.3. Chlorine ions release and intermediates from PCP dechlorination transformation  

Chlorine ions were continuously released during the process of PCP transformation (Fig. 3). After 19 d reaction, 0.021 mM and 0.019 mM of PCP were transformed at the presence of S-TFA (Fig. 3a) and S-TGA (Fig. 3b), respectively. Accordingly, 0.021 mM and 0.022 mM Cl⁻ were released at the same reaction points. For instance, approximately one mole Cl⁻ was obtained when one mole of PCP was transformed. Results showed that the presence of Fe(II) and oxalic acid promoted the release of Cl⁻ (Fig. 3). When 1 mM Fe(II) was added to colloids from S-TFA and S-TGA, the released Cl⁻ concentration increased from 0.021 mM and 0.019 mM up to 0.030 and 0.036 mM, respectively. When 1 mM oxalic acid was added, the generated Cl⁻ ions increased from 0.021 mM and 0.019 mM up to 0.030 and 0.037 mM, respectively. The same results were obtained for PCP transformation experiments from other soil colloids (data not showed).

To analyze the intermediates, the reductive transformation reaction lasted 30 d in the suspension of S-TGA in the presence of added 1.0 mM Fe(II). The intermediates during PCP reductive transformation, such as tetrachlorophenol (TeCP) and trichlorophenol (TCP), were detected by GC-MS (data not showed).

4. Discussions

4.1. Effects of Fe(II) and oxalic acid on PCP transformation

The removal of PCP on the surface of soil colloids was mainly due to the existence of Fe in soil colloids. Minerals containing Fe(II) have been found to degrade several kinds of priority pollutants, including halogenated hydrocarbons (McCormick et al., 2002; Lee and Batchelor 2002b), nitroaromatic compounds (Klausen et al., 1995), and inorganic ions (White and Peterson, 1996). Moreover, the reaction suspension containing Fe(II) species and various iron oxides have high reactivity with respect to chlorinated hydrocarbons under anoxic conditions (Amonette et al., 2000; Pecher et al., 2002). In our samples, abundant Fe was observed in the ten soil colloids (Section 3.1), which was dominated...
by DCB-Fe and amorphous-Fe. DCB-Fe composes of crystalline iron (hydro)oxides, amorphous iron (hydro)oxides, as well as complexed-Fe (Agbenin and Olojo, 2004; Pansu and Gautheyrou, 2006), and amorphous-Fe and complexed-Fe are more active than other forms (Berlier et al., 2005). As to the soil colloids used, some structural or adsorbed Fe(II) were formed during formation process of soils due to the microbial reduce action and dissolved organic matters (Ezzaïm et al., 1999). Along with the formation of Fe(II), the unreactive sites on the surface of soil colloids could be conversed to reactive Fe(II) sites with high electron density of protonated *≡FeIIIFeIIOH2* +, i.e. one type of surface-bound Fe(II) species, as shown in Fig. 4, which showed the variation of surface-bound Fe(II) concentration on S-RF. Surface-bound Fe(II) could also be generated when being applied to PCP transformation (date not shown) (Li et al., 2008). The formed surface-bound Fe(II) species on the surface of soil colloids are more active of deoxidizing the PCP than the dissolved Fe(II) (Li et al., 2008).

The injected 1.0 mM of Fe(II) in the reaction suspension elevated the PCP transformation rate, as shown by T3 data in Fig. 2. With adding Fe(II) into the reaction suspension, Fe(II) could be adsorbed on the surface of soil colloid, and surface-bound Fe(II) formed simultaneously. Increase of surface-bound Fe(II) will lead to the increase of the density of Fe(II) on the colloid surface (Fig. 4), which led to elevated PCP transformation rate. Satapanajaru et al. (2003) reported a promoted transformation rate for metolachlor transformation when Fe(II) was added into magnetite-metolachlor suspension. This further confirmed the function of Fe(II) in PCP transformation process.

Fe(II) can also be generated in soil by chemical reductive dissolution of iron oxide with polycarboxylic acid existing in soil, especially in rhizosphere (Roden, 2004). Adding oxalic acid into the reaction suspension also promoted the PCP transformation process, as shown by T2 data in Fig. 2. Oxalic acid, one of the natural organic acids mainly exuded by plants, has strong chelating ability with multivalent cations (Kayashima and Katayama, 2002). It was reported that oxalic acid can promote the reductive dissolution of iron oxides, and enhance the production of Fe(II) species in soil (Lee et al., 2007). With the injection of oxalic acid, Fe(II)-oxalate complexes could be formed on the surface of soil colloid, which is one type of surface-bound Fe(II). Surface Fe(II)-oxalate complexes are more active than other surface-bound Fe(II), such as *≡FeIIIFeIIOH2* (Butler and Hayes, 1998). Our group reported that surface-bound Fe(II) can enhance the PCP abiotic transformation (Li et al., 2008). Hence, the results further indicate that surface-bound Fe(II) should be an important factor affecting PCP abiotic transformation on the soil colloid surfaces.

### 4.2. Effects of soil properties on PCP transformation

Physicochemical properties of soil colloids, such as BET surface area, pH and Fe contents affected PCP transformation. Correlation of *k* values for PCP transformation with soil physicochemical properties is shown in Table 4 and Fig. 5.

**Table 4**

<table>
<thead>
<tr>
<th>Soil properties</th>
<th>T1</th>
<th>T2</th>
<th>T3</th>
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<tbody>
<tr>
<td>pH</td>
<td>0.685*</td>
<td>0.784**</td>
<td>−0.106</td>
</tr>
<tr>
<td>TOC</td>
<td>−0.363</td>
<td>−0.166</td>
<td>−0.341</td>
</tr>
<tr>
<td>Total Fe</td>
<td>0.419</td>
<td>0.012</td>
<td>0.893**</td>
</tr>
<tr>
<td>DCB-Fe</td>
<td>0.387</td>
<td>0.066</td>
<td>0.638*</td>
</tr>
<tr>
<td>Amorphous-Fe</td>
<td>−0.181</td>
<td>0.064</td>
<td>−0.233</td>
</tr>
<tr>
<td>Complexed-Fe</td>
<td>−0.238</td>
<td>−0.009</td>
<td>−0.511</td>
</tr>
<tr>
<td>BET</td>
<td>0.789**</td>
<td>0.750**</td>
<td>0</td>
</tr>
</tbody>
</table>

*Correlation is significant at the 0.05 level; **Correlation is significant at the 0.01 level (2-tailed). T1, T2 and T3 were the same as in Table 3.*
(Table 4) showed that PCP transformations on soil colloids without (T1) and with oxalic acid (T2) were significantly and positively associated with BET and pH. In comparison, transformation on soil colloids with Fe(II) (T3) were significantly and positively related to DCB-Fe and total Fe. Additionally, Total Fe and DCB-Fe were excluded from stepwise regression models. The models indicated that BET was the primary factor affecting T1 and T2 (Fig 5a). pH was the direct factor affecting T1 and T2 (Fig 5b), and DCB-Fe was the dominant contributor to T3 transformation (Fig 5c).

The reductive transformation of PCP is a heterogeneous reaction on the surface of soil colloids. The adsorption of PCP is the first step of the reaction. Contribution of BET surface area on PCP transformation derived from the increased adsorption capacity of PCP for T1 treatment. For T2 treatment, a higher BET surface area might elevate the adsorption of oxalic acid and then enhance the formation of Fe(II) species due to complexation of oxalic acid with Fe on soil colloids (Teoh et al., 2007; Lee et al., 2007). The effect mechanism of pH on PCP transformation was attributed to completion of oxalic acid to form Fe(III) species. A higher pH value can enhance the conversion of Fe(III) to Fe(II) in solution (Butler and Hayes, 1998), an increased pH value might lead to an enhanced reactivity for PCP transformation. The same results of pH effects were obtained when a brown acid soil developed from tuff (Beaujolais, France) Part II. Soil formation. Geoderma 87, 155–177.


5. Conclusions

PCP was degraded and dechlorinated on the soil colloids developed from Basalt, Sandshale and Quaternary Period red earth. PCP transformation was further accelerated at the presence of additional oxalic acid or Fe(II) solutions. The soil colloids developed from Basalt was more active for PCP transformation than other colloids. While for the soil colloids developed from Sandshale, the two paddy soil colloids were more active than other three soils from Sandshale. Effects of soil colloids and oxalic acid on PCP transformation were positively related to BET surface area of colloids. Fe-rich soil colloids and oxalic acid may be potential materials to degrade and dechlorinate organic PCP pollutants in subtropical and tropical soils.

Acknowledgement

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