

# Effects of pH and Cadmium on Tetracycline Sorption to Soils

Guixiang Zhang, **Xitao Liu**, Ke Sun, Ye Zhao, Chunye Lin

State Key Laboratory of Water Environment Simulation, School of Environment, Beijing Normal University, Beijing 100875, China, Email [liuxt@bnu.edu.cn](mailto:liuxt@bnu.edu.cn)

## Abstract

Batch sorption experiments were conducted to evaluate the sorption of tetracycline (TC) on soils as affected by pH and cadmium. Sorption isotherms of TC on soils in the presence and absence of Cd (II) were well fitted with the Freundlich equation. Sorption of TC strongly depended on environmental factors and soils characteristics. Lower pH facilitated TC sorption through cation exchange mechanism which also took place at pH above 5.5 where TC existed as zwitterion ( $H_2L^0$ ) or anions ( $HL^-$  and  $L^{2-}$ ). When pH was above 7, ligand-promoted dissolution of TC might occur due to the TC weakening the Al-O bond of aluminum oxide and Fe-O bond of iron oxide. The presence of Cd (II) increased TC sorption on soils, which was resulted from the decrease of equilibrium solution pH caused by  $Cd^{2+}$  exchange with  $H^+$  ions of soil surfaces. The increase of TC sorption was also related to the formation of TC-Cd complexes and the bridge provided by  $Cd^{2+}$  between the soil and TC.

## Key Words

Sorption, tetracycline, pH; cadmium, soil

## Introduction

Sorption is an important process that affects the fate, transportation, bioavailability and toxicity of contaminants. TC is predominantly sorbed on soil clays and humic substances either mask sorption sites on clay surfaces or inhibit interlayer diffusion of TC. Sorption of TC decreased with increasing pH and sorption by clay appeared to be increased in the presence of Ca versus Na (Figueroa *et al.* 2004; Kulshrestha *et al.* 2004; Figueroa and MacKay 2005; Pils and Laird 2007). TC has multiple ionizable functional groups (Sassman and Lee 2005), sorption of TC significantly depends on environment elements and the properties of soil samples.

On the other hand, soils usually contain other contaminants such as heavy metals, which may affect sorption of TC. In recent years, some researchers focus on the interaction between metal ions and TC (Wang *et al.* 2008; Jia *et al.* 2008). Cadmium (Cd) as a nonessential element can result in adverse effects on animals and humans (Tu *et al.* 2007). High contents of Cd may be present in livestock additives because of contamination of mineral supplements (Nicholson *et al.* 2003). Thus, Cd can often coexist with TC, which may affect behavior of TC, however, little attention is paid to this possibly. The objective of this study is to investigate the sorption isotherms of TC on soils as affected by Cd and pH.

## Materials and methods

### *Chemicals and soils*

Tetracycline hydrochloride (98% purity) was obtained from Alfa Aesar. TC stock was prepared in methanol and stored at 4°C in the dark and refreshed every month. Calcium chloride anhydrous, sodium azide, oxalic acid dihydrate,  $CdCl_2 \cdot 5/2H_2O$ , HCl and NaOH were all reagent grade. Acetonitrile and methanol were HPLC grade. Solutions were prepared with high-purity water (18M $\Omega$ , Millipore Simplicity 185).

Three air-dried soils were gently crushed to pass through a 0.25 mm sieve. Three soil samples (0-20 cm) were collected from East Xinzhuang (Soil 1), North Tanggu Farm (Soil 2) and Northeast Dougu Town (Soil 3) respectively. The properties of soils were shown in Table 1. Cation exchange capacity (CEC) was determined by the method of ammonium acetate exchange. Organic carbon (OC) contents were determined using an Elementar Vario EI elemental analyzer (Germany) after the acid-treatment (1 M HCl). Particle size distributions were determined by laser particle size analyzer (Mastersizer 2000, Malvern Instrument Ltd. Malvern, UK). The content of total Fe and Al oxides in sediments and soils were determined by HF-HClO<sub>4</sub>-HCl.

**Table1. Some physical and chemical characteristics of the selected sediment and soil samples.**

Samples	pH (1:2.5)	OC (wt.%)	CEC (cmol/kg)	Fe <sub>2</sub> O <sub>3</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	Particle size distribution (wt.%)			
						<0.002 mm	0.002-0.02 mm	0.02-0.25 mm	0.25-2 mm
Soil1	8.63	1.14	23.40	38.94	64.84	5.40	25.74	57.69	11.17
Soil2	8.39	1.90	24.06	38.66	67.02	1.20	16.54	57.69	11.17
Soil3	8.64	1.15	21.61	35.29	69.94	11.37	38.23	46.62	3.78

### Sorption experiments

All experiments were conducted in 30 ml Nalgene polypropylene centrifuge tubes. According to preliminary experiment, 24 h was chosen as the equilibration time and the loss of TC was negligible. The prepared TC solution contained 0.01 M CaCl<sub>2</sub> to maintain a certain ionic strength and 1.5 mM sodium azide to inhibit biological activity, and was adjusted to pH 5.5 with HCl or NaOH. Twenty-five milliliter of different concentrations (from 5 to 150 mg/L) of TC solution with and without 10 mg/L of Cd (II) was added into each tube containing about 0.1 g soil. Soil 3 was selected to investigate the effect of pH on TC sorption with and without Cd (II) and were performed with a single TC concentration (30mg/L). Different pHs varying from 3.5 to 9.5 in one-unit increments were adjusted with 0.1 M HCl or 0.1 M NaOH. Sorbate-free control and Sorbent-free control tubes were prepared in the same manner. Duplicate experiments were conducted for all samples.

Concentrations of TC were determined by high-performance liquid chromatography system equipped with a UV detector (Germany Lumtech K-2600, Lumiere Tech Ltd.) using Inertsil ODS-3 C18 column (5 μm, 250×4.6 mm). Samples were eluted isocratically with a mixture of acetonitrile (23%) and 10 mM oxalic acid (77%), flowing at 1.0 ml/min. TC was measured by absorption at 360 nm. The amount of TC adsorbed was calculated by the difference between the amount of TC added initially and that remained in the aqueous after equilibration.

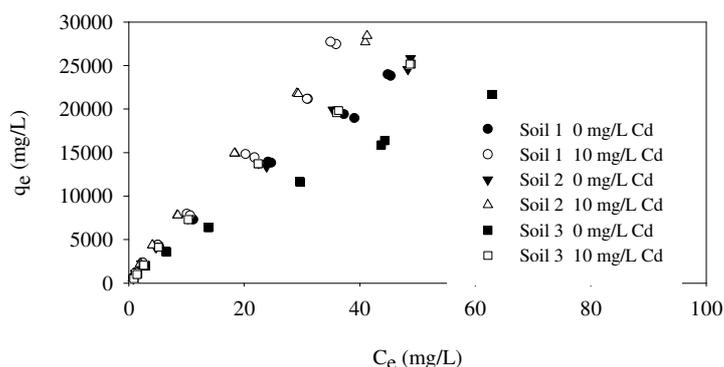
## Results and Discussion

### Sorption isotherms

The Freundlich isotherm model commonly used for quantifying equilibrium sorption of hydrophobic organic compounds (HOCs) by soils has the following forms:

$$q_e = K_F C_e^n \quad (1)$$

where  $q_e$  is the solid-phase concentration (mg/kg) and  $C_e$  is the liquid-phase equilibrium concentration (mg/L).  $K_F$  is the sorption capacity-related parameter ((mg/kg)/(mg/L)<sup>n</sup>) and  $n$  is the isotherm linearity index. Figure 1 shows the sorption isotherms of TC on soils in the presence and absence of Cd (II) at pH 5.5. The Freundlich



**Figure 1. Tetracycline sorption isotherms on three soils in the presence and absence of Cd.**

equation fits the sorption isotherms of TC with high correlation coefficients ( $r^2 = 0.997-0.999$ ) (Table 2), which suggests that the Freundlich equation can be used to sufficiently describe TC sorption to the soils with and without Cd (II). The organic carbon-normalized sorption coefficient ( $K_{FOC}$ ) was calculated by dividing  $K_F$  values by the fraction of organic carbon ( $F_{oc}$ ). The single point  $K_{oc}$  (L/kg) was calculated by the following equation:

$$K_{oc} = K_{FOC} C_e^{n-1} \quad (2)$$

**Table 2. Freundlich sorption model coefficients for TC adsorption on soils in the presence and absence of Cd (II)**

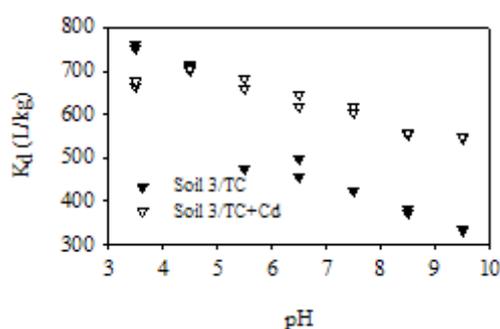
Samples	Cd (mg/L)	$K_F^A$	$K_{FOC}$	$n^B$	$r^2$	$N^C$	Concentration-dependent $K_{oc}$		
							$C_e=0.005$ (mg/L)	$C_e=0.05$ (mg/L)	$C_e=0.5$ (mg/L)
Soil1	0	1106±44	970	0.826±0.025	0.999	16	2439	1633	1094
	10	1425±91	1250	0.999±0.049	0.997	16	1257	1253	1251
Soil2	0	1127±62	593	0.800±0.015	0.998	16	1711	1080	681
	10	1364±55	718	0.816±0.012	0.999	16	1903	1246	816
Soil3	0	778±21	676	0.802±0.007	0.999	16	1930	1223	775
	10	1072±43	932	0.813±0.011	0.999	16	2510	1632	1061

<sup>A</sup>95% confidence interval of  $K_F$ ; <sup>B</sup>95% confidence interval of  $n$ . <sup>C</sup>number of observations;

The data in Table 2 show that the  $n$  values for TC by the soils varied from 0.800 to 0.826 with an average of 0.809. The differences of  $n$  values may be caused by different origins of soils. For all soil samples, higher  $C_e$  concentrations would result in lower  $K_{oc}$  values because of nonlinear sorption. When  $C_e$  was at 0.005 and 0.05 mg/L, the  $K_{oc}$  values for the three soils ranged from 1711 to 2439 L/kg with average at 2027 L/kg and from 1080 to 1633 L/kg with average at 1311 L/kg, respectively. When  $C_e$  was at the higher concentration (0.5 mg/L), the values of  $K_{oc}$  were much lower, ranging from 681 to 1094 L/kg.

#### Effects of Cd and pH on sorption of TC

When pH is 5.5, TC predominantly exists as the zwitterions (Sassman and Lee 2005), Cd (II) increased the sorption of TC on the three soils (Figure 2). Figure 2 shows that the  $K_d$  values was higher at lower pHs, because the cationic TC can combine with the negatively charged sites on soil surfaces, which increase the sorption of TC.  $K_d$  values of TC for Soil 3 in the presence of Cd (II) at different pHs were also shown in Figure 2. Cd suppressed the sorption of TC on Soil 3 when pH was below 4.5, this may be due to the competition of Cd (II) with TC and TC-Cd complexes. On the other hand Cd (II) promoted the sorption of TC on Soil 3 when pH was above 5.5, this may be due to Cd (II) acting as bridge between TC and Soil 3. This result was similar to the research on cosorption of TC and Cu (II) on soils conducted by Jia *et al.* (2008).



**Figure 2. Effects of pH on TC sorption on Soil 3 in the presence and absence of Cd.**

#### Relationship between soil properties and sorption isotherm

The pHs and CEC for three soils were similar, the differences of sorption capacities indicated that other properties played important roles. This experiment revealed that TC was less favor to be sorbed to Soil 3 which had obviously higher clay than others. A probable reason was that more ligand-promoted dissolution was occurring during TC sorption to Soil 3. Although Soil 1 and Soil 2 had more iron oxide content, they had less amount of aluminum oxide than Soil 3 (Table 1), which might result in the higher sorption capacity for Soil 1 and Soil 2. This result was consistent with sorption of TC to aluminum and iron hydroxides decreasing with increasing pH when pH was up to 7 (Gu and Karthikeyan 2005).

#### Possible sorption mechanism of TC in the absence and the presence of Cd(II)

Cation exchange has been reported as an important mechanism for TC sorption at acidic condition. pHs decreased with increasing concentration of TC (data were not shown), which suggested that cation exchange took place above pH 5.5, as the negative and positive charges on TCs were spatially separated and they might play their respective roles similar to that of soil cation and anion exchange sites (Sassman and Lee 2005). When pH was above 7, sorption of TC to aluminum and iron oxides decreased with increasing pH

because of ligand-promoted dissolution. Ligand-promoted dissolution was more significant for aluminum oxides than for iron oxides (Gu and Karthikeyan 2005). A possible explanation for the increase of TC sorption in the presence of Cd (II) could be that the equilibrium solution pHs were lower than those in the absence of Cd (II). The pH decreased in the equilibrium solution when Cd (II) was added, which was caused by  $\text{Cd}^{2+}$  exchanging with  $\text{H}^+$  ions of soil surfaces. The cationic Cd could also combine with the negative charge sites on the soil surfaces, acting as a bridge between TC and soil particles (Pils and Laird 2007; Jia *et al.* 2008; Wang *et al.* 2008). Another reason might be related to the formation of TC-Cd complexes as well. The predominant TC species at solution pH between 6 and 8 were  $\text{H}_2\text{L}^0$ ,  $\text{HL}^-$ , and  $\text{L}^{2-}$  (Sassman and Lee 2005), which could strongly combine with the Cd (II) to form  $\text{CdH}_2\text{L}^{2+}$ ,  $\text{CdHL}^+$ , and  $\text{CdL}$  complexes. These TC-Cd complexes had less negative surface charge and more easily adsorbed on soil surfaces than TC itself at high pH conditions.

## Conclusion

Sorption of TC on soils as affected by Cd (II) and pH were investigated in this study. Sorption of TC decreased with increasing pH, and basic conditions did not facilitate TC sorption, which suggested TC introduced into alkali soils would increase its environmental risk. When pH was above 7, aluminium and iron oxides might increase the mobility and bioavailability of TC due to ligand-promoted dissolution in soil pore waters. Cd enhanced TC sorption on soils at environmentally relevant pH values, thus reducing the mobility of TC. The results in this study can be potentially valuable in predicting the fate, bioavailability and risk of TC in soils. In addition, sorption of TC by different components of organic matter in soils needs further investigations.

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