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Ofloxacin sorption in soils after long-term tillage: The contribution of organic and mineral compositions

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HIGHLIGHTS

- Mineral compositions tend to be similar after tillage.
- Increased SOM decreases OFL sorption for soils from the same geological location.
- Tillage activities or dense vegetations greatly decrease OFL sorption.
- The summed sorption of individual soil components is higher than the intact soil.
- Soil should be treated as a dynamic environmental matrix for antibiotic sorption.

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ABSTRACT

Intensive human activities in agricultural areas resulted in significant alteration of soil properties, which consequently change their interactions with various contaminants. This process needs to be incorporated in contaminant behavior prediction and their risk assessment. However, the relevant study is missing. This work was designed to examine the change of soil properties and ofloxacin (OFL) sorption after tillage. Soil samples were collected in Yuanyang, Mengzi, and Dianchi areas with different agricultural activities. Although the mineral compositions of soils from Yuanyang and Dianchi differed greatly, these compositions are similar after tillage, especially for paddy soils. Soil pH decreased generally after OFL sorption, suggesting that ion exchange of OFL with protons in soil organic matter (SOM) was important for OFL sorption. However, a positive relationship between SOM and OFL sorption was not observed. On the contrary, increased SOM decreased OFL sorption when soils from the same geological location were compared. Generally speaking, tillage activities or dense vegetations greatly decreased OFL sorption. The higher OFL sorption in B horizon than A horizon suggested limited leaching of OFL through soil columns. The summed sorption calculated based on the sorption of individual soil components and their percentages in soils was higher than the intact soil. This phenomenon may be understood from the interactions between soil components, such as the coating of SOM on mineral particles. This study emphasizes that soil should be treat as a dynamic environmental matrix when assessing antibiotic behaviors and risks, especially in the area with intense human activities.

1. Introduction

The wide application of antibiotics has resulted in their ubiquitous presence in the environment, such as surface water, seawater, groundwater, soils, and sediments (Nikolaou et al., 2007; Kemper, 2008; Thiele-Bruhn, 2003). For example, as high as 1560 ng/g ofloxacin (OFL) was detected in the sediments of the Pearl Rivers (Yang et al., 2010). Lots of research attention have been attracted regarding the negative effects of antibiotics to ecological systems and the frequently reported drug resistant genes (Cirz et al., 2005; Dhar and McKinney, 2007). Proper assessment of antibiotic risks requires a comprehensive understanding of their environmental behaviors. The interactions between antibiotics and environmental media, primarily soil particles, are essential for the above purpose. In addition, soil is the environmental matrix with the most abundance of microorganisms, and a very important zone for the development of drug resistant genes. Thus, the occurrence of antibiotics in soil system and antibiotic–soil interaction has been the research hotspot recently.

Previous studies have suggested that both organic and inorganic compositions of soil particles are important for antibiotic sorption (Wu et al., 2014). It was also reported that different soil compositions have distinct sorption characteristics to antibiotics (Peterson et al., 2009). During the chemical weathering of soils as well as the biological activities in soil systems, soil compositions will be changed, which consequently alter soil–antibiotic interactions. Thus, soils could not be

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Table 1
Selected soil and mineral properties.

	pH_{zpc}	CEC	BET	Mineral analysis									Elemental analysis						
		cmol(+)/kg	m^2/g	QZ	MS	HB	KL	ML	CT	OH	HM	CC	N	C	H	S	O	C/H	C/(N + O)
Y-N	**2.24**	**2.12**	**33.9**	**43.4**	**35.2**	**12.6**	**5.3**	**nd**	**nd**	**1.0**	**nd**	**2.5**	**0.06**	**0.45**	**0.97**	**0.08**	**7.90**	**0.04**	**0.08**
Y-P	2.87	6.68	18.4	45.1	27.0	10.8	8.3	4.7	nd	1.0	nd	3.1	0.18	1.93	1.01	0.04	8.38	0.16	0.30
Y-D	2.78	4.83	18.3	46.0	30.7	8.4	6.5	4.4	nd	1.0	nd	3.0	0.19	1.94	1.02	0.04	8.59	0.16	0.29
M-N	**3.69**	**5.33**	**82.0**	**31.8**	**21.2**	**nd**	**23.4**	**7.4**	**nd**	**1.0**	**11.4**	**3.8**	**0.23**	**2.66**	**1.80**	**0.07**	**13.96**	**0.12**	**0.25**
M-G	3.63	8.18	35.0	24.8	15.0	nd	30.0	9.5	nd	1.0	16.3	3.4	0.18	1.95	1.71	0.05	15.51	0.10	0.17
M-A	5.34	8.16	22.6	32.1	18.3	nd	23.4	12.8	nd	1.0	5.1	7.3	0.93	11.87	2.39	0.09	24.33	0.41	0.62
M-B	3.35	9.69	65.8	28.4	14.1	nd	26.1	22.5	nd	1.0	5.0	2.9	0.32	2.85	1.85	0.09	14.43	0.13	0.26
B-N	**7.36**	**13.94**	**65.6**	**17.8**	**19.5**	**nd**	**27.4**	**10.9**	**13.0**	**1.0**	**8.3**	**2.1**	**0.05**	**1.53**	**1.54**	**0.05**	**15.30**	**0.08**	**0.13**
B-P	2.89	13.74	30.0	49.1	25.5	nd	8.8	6.1	nd	1.0	6.5	3.0	0.22	2.16	1.00	0.06	6.79	0.18	0.41
B-D	6.66	12.78	22.7	48.8	21.2	nd	11.3	6.8	nd	1.0	6.5	4.4	0.32	3.53	1.06	0.19	9.22	0.28	0.49
B-T	3.54	7.81	2.62	41.1	21.6	nd	9.5	7.4	nd	nd	nd	20.4	1.27	22.04	3.01	0.38	17.03	0.61	1.59

The abbreviations for mineral compositions: QZ (quartz); MS (muscovite); HB (hydrobiotite); KL (kaolinite); ML (montmorillonite); CT (calcite); OH (octahedrite); HM (hematite); and CC (crystalline carbon).

treated as static environmental media for antibiotics sorption. The change of soil properties (such as soil compositions) should be incorporated when predicting the environmental behavior of antibiotics. This is especially true when human behavior is involved. For example, long-term intensified agricultural activities altered greatly soil properties, such as degree of clay dispersion, aggregate sizes, SOM stability, as well as mineral elemental contents (Abdollahi et al., 2014; Blazewicz-Wozniak et al., 2008).

Soil organic matter (SOM) is the soil component with the primary interest when the sorption mechanisms of organic contaminants are investigated (Mechlinska et al., 2009; Pan et al., 2007). The interactions between SOM and antibiotics are reported to be significant (Bao et al., 2009; Pan et al., 2012a, 2012b). But different from hydrophobic organic contaminants, the sorption of antibiotics on mineral particle was also important. The mineral fractions usually showed comparable or even higher sorption than organic matter. SOM, such as low-molecular-weight organic acids, could coat on mineral particles and compete with antibiotics for sorption sites (Zhang and Dong, 2008). We have presented that the organic matter-removed soil particles showed higher sorption than the original soil (Hou et al., 2010). The sorption of antibiotics on different mineral fractions will be important for predicting antibiotic behavior. Therefore, both organic and mineral composition change during tillage activities will alter antibiotic sorption characteristics on soil particles. However, previous studies mostly focus on the property change of organic fractions, with limited interest on soil mineral compositions.

This study is specifically designed to investigate antibiotic sorption in soils after tillage. The same soil without tillage will also be collected for reference. Both organic and inorganic compositions will be characterized and be incorporated in understanding antibiotic sorption mechanisms. OFL will be used as a model antibiotic because of its wide application (Pico and Andreu, 2007; Van Wierene et al., 2012), high-concentration occurrence in the environment (Yang et al., 2010), and strong sorption in soils/sediments in comparison to other antibiotics (Cirz et al., 2005). This study will provide useful information for antibiotic environmental behavior prediction and risk assessment.

2. Experimental section

2.1. Preparation of the adsorbents

Soil samples with different tillage activities were collected in different locations of Yunnan province, southwest of China. The common tillage behavior in these sampling areas generally involves the input of soil amendments and ploughing. Yuanyang terrace area is a very famous farming area in Yunnan. The terrace area has been cultivated for more than one thousand years. Both soils from paddy field (Y-P) and dry farmland (Y-D) were collected in the area of latitude 102.74178–102.74451 and longitude 23.07307–23.07341. Natural soil (Y-N) from the same region without cultivation was also collected in the mountain area at higher elevation for comparison. A large area of panax pseudo-ginseng planting was located in Mengzi mountain area. Panax pseudo-ginseng planting was known as an intensified farming process with massive application of fertilizers and pesticides. Three-year Panax pseudo-ginseng planting generally involves 8–10 years fallow period before the next cultivation. Soil samples before (M-N) and after (M-P) three-year panax pseudo-ginseng planting were collected. In addition, soil A layer (M-A) and B layer (M-B) were collected in the mountain area without

Table 2
Fitting results of OFL sorption isotherms using Freundlich equation.

	$\log K_F$	SE	n	SE	$r_{adj}{}^2$	K_d(L/kg)		pH_a	SE	pH_o
						$C_e = 0.1C_s$	$C_e = 0.01C_s$			
Y-N	**3.25**	**0.01**	**0.461**	**0.014**	**0.992**	**75.8**	**263**	**6.51**	**0.10**	**5.55**
Y-P	3.14	0.04	0.421	0.048	0.883	46.6	177	6.73	0.09	6.19
Y-D	3.23	0.02	0.446	0.022	0.969	67.8	243	6.78	0.08	5.41
M-N	**3.60**	**0.04**	**0.524**	**0.040**	**0.928**	**250**	**748**	**6.38**	**0.16**	**5.45**
M-G	3.56	0.04	0.463	0.039	0.926	158	544	6.68	0.10	6.31
M-A	3.31	0.03	0.627	0.040	0.955	234	552	6.97	0.05	6.93
M-B	3.57	0.02	0.531	0.025	0.971	239	705	6.60	0.12	6.32
B-N	**2.41**	**0.05**	**1.080**	**0.053**	**0.970**	**409**	**340**	**8.04**	**0.20**	**8.21**
B-P	3.21	0.03	0.689	0.031	0.974	264	540	7.08	0.09	6.13
B-D	2.67	0.03	0.813	0.028	0.985	156	240	7.50	0.13	7.54
B-T	3.97	0.02	0.509	0.024	0.981	530	1640	6.23	0.10	5.37
B-N-M	4.27	0.02	0.336	0.020	0.961	384	1770	6.61	0.25	nd
QZ	1.42	0.02	0.478	0.022	0.970	1.3	4.2	6.80	0.11	
MS	1.85	0.05	0.404	0.049	0.836	2.2	8.7	9.40	0.22	
KL	3.35	0.02	0.380	0.019	0.965	60.5	252	6.57	0.14	
ML	4.98	0.04	0.289	0.036	0.911	1510	7780	6.11	0.21	