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Sorption of fluoroquinolones and sulfonamides in 13 Brazilian soils

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HIGHLIGHTS

- Fluoroquinolones sorption was very high ($K_d \geqslant 544$ L kg^{-1}).
- Sulfonamides sorption ranged from low to high (K_d = 0.7–70.1 L kg^{-1}).
- Soil texture and CEC were the soil attributes that mostly affected sorption.
- Ionic exchange process seems be an important sorption mechanism.
- Hydrophobic partition also plays a role in the sulfonamides sorption.

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ABSTRACT

Animal production is a leading economic activity in Brazil and antibiotics are widely used. However, the occurrence, behavior, and impacts of antibiotics in Brazilian soils are still poorly known. We evaluated the sorption behavior of four fluoroquinolones (norfloxacin, ciprofloxacin, danofloxacin, and enrofloxacin) and five sulfonamides (sulfadiazine, sulfachloropyridazine, sulfamethoxazole, sulfadimidine, and sulfathiazole) in 13 Brazilian soils with contrasting physical, chemical, and mineralogical properties. Fluoroquinolone sorption was very high ($K_d \geqslant 544$ L kg^{-1}) whereas sulfonamide sorption ranged from low to high (K_d = 0.7–70.1 L kg^{-1}), consistent with previous reports in the literature. Soil texture and cation exchange capacity were the soil attributes that most affected sorption. Cation exchange was the most important sorption mechanism for the fluoroquinolones in highly weathered tropical soils, although cation bridging and ion pairing could not be ruled out. Hydrophobic partition played an important role in the sorption of the sulfonamides, but sorption was also affected by non-hydrophobic interactions with organic and/or mineral surfaces. Sorption for both compound classes tended to be higher in soils with high Al and Fe oxihydroxide contents, but they were not correlated with K_d values. No direct effect of soil pH was seen. The fluoroquinolones are not expected to leach even in worst-case scenarios (soils rich in sand and poor in organic carbon), whereas soil attributes dictate leaching potential for the sulfonamides.

1. Introduction

Fluoroquinolones and sulfonamides are two important classes of antibiotic compounds commonly used in veterinary medicine worldwide (Karci and Balcioglu, 2009). A series of recent studies focused on their prevalence, fate, and environmental risks (Picó and Andreu, 2007; Zhao et al., 2010; Baran et al., 2011; Leal et al., 2012). Concentrations up to 0.40 mg kg^{-1} were reported for both fluoroquinolones and sulfonamides in agricultural soils worldwide, but much higher concentrations were reported in animal manure (Martínez-Carballo et al., 2007; Karci and Balcioglu, 2009; Zhao et al., 2010). In addition, storing manure contributed little to the degradation of these compounds (Lamshöft et al., 2010). Fluoroquinolones degraded slowly in soils (half-lives >60 d) (Golet et al., 2003; Boxall et al., 2006) whereas sulfonamide degradation was faster (half-lives = 18.6 and 21.3 d for sulfamethazine and sulfachloropyridazine, respectively) (Accinelli et al., 2007). The formation of non-extractable residues is most likely the main process governing dissipation of these compounds in soils, with residual concentrations persisting in the long term (Kreuzig and Höltge, 2005; Rosendahl et al., 2011).

These classes of antibiotics comprise distinct ionizable groups at relevant environmental pH values (Table 1), suggesting that mechanisms other than hydrophobic partitioning affect their sorption behavior (Sukul et al., 2008; Vasudevan et al., 2009) and that they behave quite distinctly in terms of sorption. Fluoroquinolones show high sorption to soils (K_d = 260–5012 L kg^{-1}) (Sarmah et al.,

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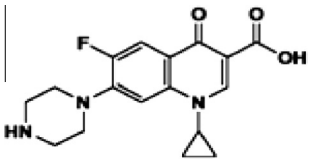
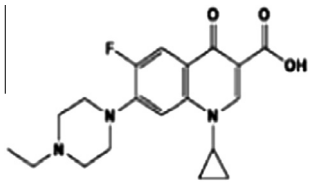
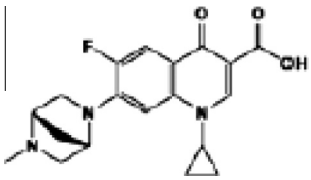
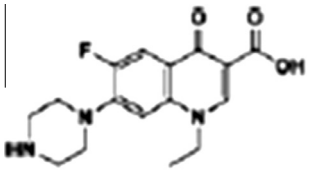
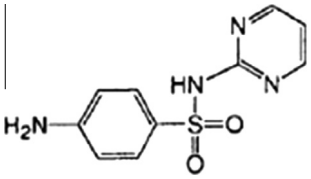
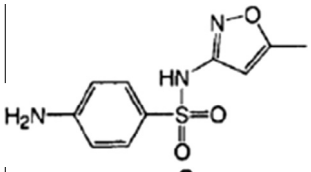
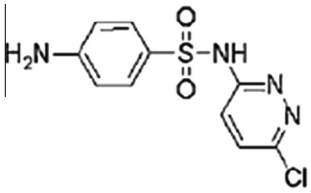
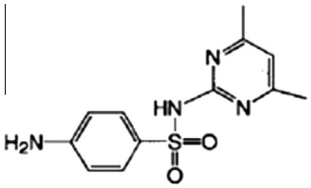
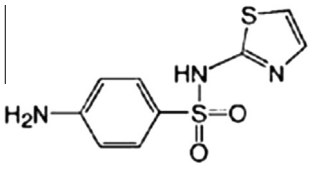
Table 1
Molecular structure and weights as well as pK_a and logK_{ow} values for the studied fluoroquinolones and sulfonamides.

Compound	Structure	Molecular Weight (g mol^{-1})	pK_{a1}*	pK_{a2}*	LogK_{ow}
Ciprofloxacin		331.4	5.90	8.89	0.4
Enrofloxacin		359.4	6.27	8.30	1.1
Danofloxacin		357.4	6.07–6.32	8.56–8.73	1.85
Norfloxacin		319.3	6.23	8.55	–
Sulfadiazine		250.3	2.00	6.40	−0.09
Sulfamethoxazole		253.3	1.60	5.70	0.89
Sulfachloropyridazine		284.7	2.00	5.90	0.31
Sulfadimidine		278.3	2.60	8.00	0.89
Sulfathiazole		255.3	2.20	7.20	0.05

* p*K*a values for fluoroquinolones from Speltini et al. (2011) and for sulfonamides from Ikehata et al. (2006).

2006; Picó and Andreu, 2007) and tend to accumulate not only in soils but also in other solid matrices, such as sewage sludge (up to 2 mg kg^{-1}, Golet et al., 2003) and river sediments (up to 1.56 mg kg^{-1}, Yang et al., 2010). By contrast, sulfonamides show low sorption to soils (K_d = 0.6–7.4 L kg^{-1}, Sarmah et al., 2006) and therefore tend to have high leaching potential. Indeed, sulfona-