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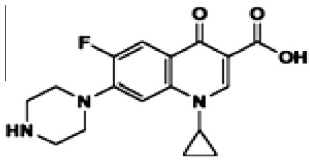
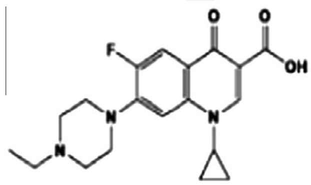
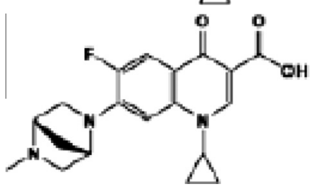
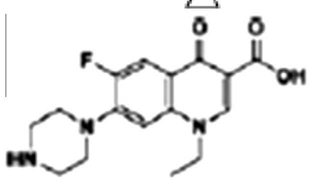
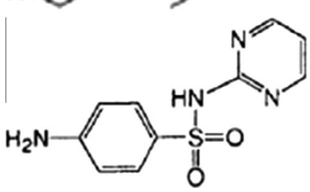
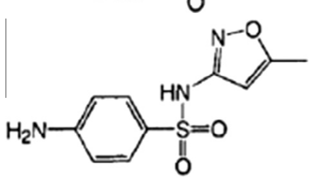
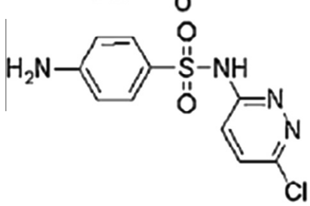
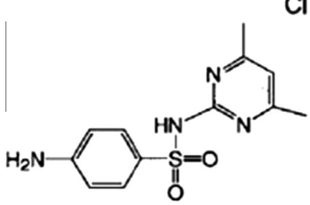
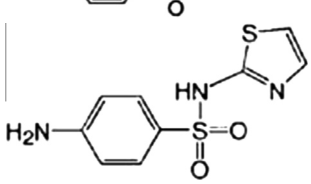
Table 1
Molecular structure and weights as well as pK_a and logK_{ow} values for the studied fluoroquinolones and sulfonamides.

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

* pKa 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, sulfonamides have been reported in groundwater samples (up to 0.47 μg L^{-1}, Hirsch et al., 1999) whereas no fluoroquinolones have been reported to date.

Sorption studies play an important role in understanding the fate and behavior of contaminants in the environment (Sukul et al., 2008). Mechanisms such as surface complexation, H-bonding, cation bridging, ion-exchange, and hydrophobic partition affect sorption of antibiotics (Tolls, 2001). Consequently, their sorption varies greatly with soil physicochemical properties, especially soil pH, quantity and quality of organic matter, and the types of minerals present (Thiele-Bruhn, 2003). For example, K_d values for enrofloxacin have been reported to vary by a factor of 30 (Boxall et al., 2004). It thus seems especially important to understand the fate of these compounds under different environmental conditions.

Brazil is one of the world's largest producers and exporters of animal products, and the use of antibiotics is substantial (Regitano and Leal, 2010). In São Paulo State, fluoroquinolones were detected at concentrations of up to 30.97 mg kg^{-1} in poultry litters and up to 26.69 μg kg^{-1} in soils, and enrofloxacin was the most commonly detected compound (Leal et al., 2012). Brazilian soils are usually highly weathered (Oxisols cover ~38% of the country), rich in 1:1 clay minerals (kaolinite) and oxides and hydroxides of Fe and Al (hematite, goethite, and gibbsite), and have mostly pH-dependent net charges (Fontes and Alleoni, 2006). This results in soils with lower cation exchange capacities (CECs) than less weathered temperate soils and should imply a lower sorption potential for cationic species that have exchange capacity as their main sorption mechanism, such as fluoroquinolones and tetracyclines (Vasudevan et al., 2009; Figueroa-Diva et al., 2010). On the other hand, in subsurface horizons where less organic carbon is present, positively charged oxide surfaces may attract considerable amounts of negatively charged antibiotic species. Moreover, neutral species may sorb more to kaolinite than to montmorillonite clays due to the larger domains for neutral species sorption on the siloxane surfaces of the kaolinites (Gao and Pedersen, 2005).

Research on the occurrence, behavior, and environmental fate of these compounds is completely lacking in Brazil. In order to address this lacuna, sorption of four fluoroquinolones (norfloxacin, ciprofloxacin, danofloxacin, and enrofloxacin) and five sulfonamides (sulfadiazine, sulfamethoxazole, sulfachloropyridazine, sulfadimidine, and sulfathiazole) to 13 Brazilian soils with distinct attributes was evaluated. Statistical analyses were performed to explore how soil attributes affect the sorption of these substances.

2. Materials and methods

2.1. Soils

Thirteen soils (0–20 cm) from São Paulo State in southeastern Brazil were collected from sites with minimum anthropogenic disturbance (native forests and forest fragments). Sites were selected from a previous study and spanned a wide range of soil attributes (Table 2) (Soares and Alleoni, 2008). The following soil attributes were evaluated: pH-$CaCl_2$, point of zero charge (PZC), organic carbon (OC), exchangeable cations (Ca, Mg, K, and Al), potential acidity (H + Al), effective and total cation exchange capacity (CEC_e and CEC_t, respectively), free iron oxide (DCBFe, dithionate-citrate-bicarbonate iron oxide), amorphous iron and aluminum oxides (AAOFe and AAOAl, acid ammonium oxalate extractable iron and aluminum oxides, respectively), texture (sand, silt, and clay), and mineralogy. Detailed information on sampling and measurement procedures is available elsewhere (Soares and Alleoni, 2008).

2.2. Reagents and standards

All fluoroquinolones (norfloxacin, NOR; ciprofloxacin, CIP; danofloxacin, DAN; and enrofloxacin, ENR) and sulfonamides (sulfadiazine, SDZ; sulfamethoxazole, SMX; sulfachloropyridazine, SCP; sulfadimidine, SDI; and sulfathiazole, STA) were HPLC grade and purchased from Sigma–Aldrich, with purity higher than 98%. The fluoroquinolone (1 mg mL^{-1}) and the sulfonamide (0.5 mg mL^{-1}) stock standard solutions were prepared in methanol (the fluoroquinolones contained 1% acetic acid), stored at −18 °C in the dark, and used within 90 d. Ultra-pure water was used to prepare all aqueous solutions. Organic solvents were all HPLC grade. Calcium chloride ($CaCl_2$) and formic acid (CH_2O_2) were analytical grade.

2.3. Sorption experiments

Preliminary tests were carried out to evaluate the stability of the compounds, sorption to tube walls, adequate soil-to-solution ratios, and equilibration time. No significant losses were found (<5%, data not shown), suggesting no biodegradation of the compounds. The soil-to-solution ratios adopted were 1:15 (2 g of soil to 30 mL of solution) for the fluoroquinolones and 1:2 (2.5 g of soil to 5 mL of solution) for the sulfonamides. Sorption potentials were evaluated in triplicate at a single concentration of 6.0 and 1.0 mg L^{-1} for the fluoroquinolones and the sulfonamides, respectively, prepared in 0.01 mol L^{-1} $CaCl_2$. This corresponded to 90 and 2 mg kg^{-1} of soil for the fluoroquinolones and sulfonamides, respectively. These concentrations are much higher than those reported in soils (up to 400 μg kg^{-1} of soil) (Baran et al., 2011; Leal et al., 2012), but were the lowest concentrations that allowed analytical detection. In addition, using the Freündlich sorption coefficients (K_f values) would be of limited value because it would not allow direct comparisons between soils, since antibiotic sorption is concentration dependent (i.e. not linear or $N \neq 1$). A single concentration approach was thus chosen, following Vasudevan et al. (2009) and Figueroa-Diva et al. (2010).

After solutions were added, tubes were horizontally shaken (200 rpm) for 24 h, centrifuged for 10 min (2620*g*), and the supernatants then syringe filtered (0.45 μm) prior to quantification of the soil solution concentration at equilibrium (C_e) by liquid chromatography (HPLC). The centrifuge tubes were covered with aluminum foil to prevent light-induced degradation during shaking. The amounts of antibiotics sorbed (S) were calculated as the difference between the initial (C_i) and equilibrium concentrations, taking into account the soil-to-solution ratio. K_d values were calculated as follows: $K_d = S/C_e$.

2.4. HPLC analysis

The instrument (HPLC from Agilent, 1200 series) was equipped with a quaternary pump, DAD and FLD detectors, and an automated injection system. The column (ACE C18, 250 × 4.6 mm, 5 μm) was kept at 25 °C and the injection volume was 50 μL. For the fluoroquinolones, the mobile phase was composed of 72% formic acid at 0.1% (solvent A) and 28% acetonitrile (solvent B). The flow rate was 1.0 mL min^{-1} and fluorescence wavelengths were set at 280 and 450 nm for excitation and emission, respectively. For the sulfonamides, the mobile phase consisted of 60% water (solvent A) and 40% acetonitrile (solvent B) containing 0.1% formic acid. The flow rate was 0.5 mL min^{-1} and diode array wavelength was set at 265 nm. The elution in both cases was isocratic.

2.5. Statistical analyses

Analysis of variance (ANOVA) was adopted to contrast K_d values, log transformed. The mean values were compared by Tukey

Table 2
Soil properties.

Soils	Classification[a]	$pHCaCl_2$	OC	P	K	Ca	Mg	Al	H + Al	CEC_t[b]	CEC_e[c]	AOFe[d]	AOAl[d]	DCBFe[e]	Clay	Silt	Sand	Mineralogy[f]
			$g\ kg^{-1}$	$mg\ kg^{-1}$	$mmol_c\ dm^{-3}$							$g\ kg^{-1}$						
LVA-1	Typic Hapludox	3.7	12.4	2.0	0.5	1.3	0.7	9.8	14.4	35.7	16.9	1.72	0.81	19.3	181	40	779	Kt
LVef	Rhodic Eutrudox	6.9	95.6	49.2	5.2	28.8	25.2	1.2	3	52.2	62.2	14.87	8.61	185.2	684	207	109	Kt,Gb
PVA-1	Arenic Hapludult	5.1	6.7	1.8	0.3	2.6	0.9	1.1	3.2	32.0	7.0	0.23	0.2	3.5	60	100	840	Kt
PVA-5	Typic Hapludalf	5.7	41.0	22.5	3.6	50.3	14	0.8	14.2	217.5	82.1	3.64	2.31	45.7	366	448	186	Kt, Il, HIV
RQ	Typic Quartzipsamment	3.8	9.6	1.1	0.4	2.2	0.9	4.2	9.2	27.6	12.6	0.33	0.22	3.0	80	40	880	Kt
RL	Lithic Udordent	4.8	26.2	6.7	1.0	22.9	8.1	1.0	10.6	153.2	42.6	0.78	0.43	7. 5	142	346	512	Il, HIV
NX	Typic Hapludult	5.1	54.3	9.4	1.6	45.9	18.2	1.3	22.2	125.2	87.9	8.25	5.49	84.5	345	182	473	Kt, Gb
NVef	Kandiudalfic Eutrudox	5.2	65.6	10.3	4.5	41	14.3	1.3	36.4	107.2	96.2	15.3	9.92	192.2	658	267	75	Kt, Gb
GM	Typic Eutraquox	3.9	213.4	14.8	1.2	5.1	3.1	41.0	124.2	109.9	133.6	0.33	0.79	4.9	476	380	144	Kt
CX	Typic Dystrochept	3.7	29.2	4.6	1.2	3.3	2.0	16.2	28.3	56.9	34.8	1.63	0.79	19.3	243	101	656	Kt
SX	Arenic Albaqult	4.8	21.6	3.0	1.3	13.4	7.8	1.5	12.1	100	34.6	2.25	1.82	18.6	204	347	449	Kt
TC	Arenic Hapludalf	4.5	9.8	1.6	1.1	3.5	1.4	1.3	5.7	39.2	11.7	0.61	0.43	8.2	40	240	720	Kt, Il, HIV
MT	Typic Argiudoll	5.4	57.8	19.2	2.4	82.1	20.1	1.1	33.3	207.8	137.8	7.19	5.09	113.3	543	251	206	Kt

[a] USDA Soil Taxonomy (Soil Survey Staff, 1999).
[b] CEC_t = total cation exchange capacity.
[c] CEC_e = effective cation exchange capacity.
[d] Iron and aluminium oxide contents extracted by acid ammonium oxalate solution.
[e] Iron content extracted by sodium dithionite- citrate-bicarbonate solution.
[f] Kt = kaolinite; Gb = gibbsite; Il = Ilite; HIV = hydroxy-interlayered vermiculite.

test ($p < 0.05$). The software R (R Development Core Team, 2012) was used. Simple linear regression (SLR) was also performed in order to relate soil attributes to K_d values (log basis).

3. Results and discussion

3.1. Fluoroquinolone sorption

Sorption of the fluoroquinolones was very high in all soils ($K_d \geqslant 544.2\ L\ kg^{-1}$) (Table 3) and corresponded to at least 84% of the amount applied, even in soils with high sand content ($\geqslant 840\ g\ kg^{-1}$), low OC content ($\leqslant 9.6\ g\ kg^{-1}$), and mostly kaolinite in the clay fraction, such as the PVA1 and RQ soils (Tables 2 and 3). Norfloxacin, ciprofloxacin, and ofloxacin sorption was also fast (less than 24 h) and high ($K_f = 7943–12309\ \mu g^{1-N}\ (cm^3)^N\ g^{-1}$) in a wetland soil that received contaminated wastewater (Conkle et al., 2010).

Overall, norfloxacin showed the highest sorption potential to the soils, whereas the enrofloxacin showed the lowest. Mean K_d values ranged from 42215.2 to 132572.3 $L\ kg^{-1}$ and median K_d values ranged from 11952.1 to 20927.5 $L\ kg^{-1}$ (Table 3). These values are mostly higher than those reported in the literature (260–5612 $L\ kg^{-1}$, Sarmah et al., 2006), suggesting a stronger affinity of fluoroquinolones to tropical soils. Although fluoroquinolone sorption is concentration dependent and tends to decrease at higher concentrations (Conkle et al., 2010), our results showed consistent higher K_d values in a scenario of comparable (20–100 $mg\ kg^{-1}$, Uslu et al., 2008) or slightly higher (20–80 $mg\ kg^{-1}$, Conkle et al., 2010) initial concentrations, thus providing strong evidence of their higher affinity to our soils.

This result was not expected, since fluoroquinolone sorption to kaolinite, which is very abundant in our soils, should be substantially lower than to montmorillonite, given its much smaller surface area ($\sim$22 versus 523 $m^2\ g^{-1}$, respectively) and CEC ($\sim$30 versus 800 $mmol_c\ kg^{-1}$, respectively), and those soil attributes have a positive impact on sorption when cation exchange is the dominant process. Essington et al. (2010) found that sorption to kaolinite was substantially lower than to montmorillonite for chlortetracycline, an antibiotic with sorption also governed by the ion exchange process. Wu et al. (2010) reported that ciprofloxacin sorption to montimorillonite was instantaneous and driven by cation exchange. Therefore, our results may be explained by the fact that sorption is not necessarily limited by the amounts of exchangeable sites available, which are usually lower in the tropical soils, but rather by the number of fluoroquinolone cationic species available (due to our lower pH values). As an example, the CEC_e of the PVA1 (the soil with the least charge) corresponded to $7 \times 10^{-3}\ mmol_c\ g^{-1}$ of soil (assuming soil density equals 1.0 $g\ cm^{-3}$), whereas the amount of ciprofloxacin sorbed corresponded to $2.67 \times 10^{-4}\ mmol_c\ g^{-1}$ of the same soil (assuming that only the cationic species were sorbed), which is an order of magnitude smaller than the amount of sites available. Accordingly, Vasudevan et al. (2009) also obtained high K_d values (300–45000 $L\ kg^{-1}$) for ciprofloxacin at pH 4.0.

The above results rule out leaching as a major process in the environmental fate of fluoroquinolones. However, these compounds may still reach aquatic environments through erosion, a common process at our study sites due to intense summer rainfall. Indeed, low concentrations of flumequine, nalidixic, and oxolinic acid (up to 32 $\mu g\ kg^{-1}$) were detected at 80 cm or deeper in sediments of the Seine River dating back to the early 1960s (Tamtam et al., 2011), reinforcing the ideas that fluoroquinolones tend to accumulate over the long term and that low concentrations can persist and pose a risk to aquatic organisms (Picó and Andreu, 2007).

CEC_t ($r = 0.79–0.84$, $p < 0.01$) and sand content ($r = -0.80$ to -0.86, $p < 0.01$) (Table 4) were the soil attributes most strongly correlated to the sorption coefficients (K_d), suggesting cation exchange as a major sorption mechanism. Fluoroquinolones are amphoteric compounds with two relevant ionizable functional groups, the acid 3-carboxyl group ($pK_{a1} = 5.9–6.3$) and the basic N-4 in the piperazine substituent ($pK_{a2} \sim 8.0$) (Table 1) (Picó and Andreu, 2007). Therefore, except for the LVef due to its higher pH value (6.9), most fluoroquinolone molecules (>61%, data not shown) are present as cationic species at natural pH values ($\leqslant$5.7) and can be electrostatically attracted to negatively charged sites of the soils (Vasudevan et al., 2009). However, cation bridging involving the dissociated carboxyl group of the zwitterionic species may also play an important role in their sorption, although ion-pairing could not be ruled out. These mechanisms are supported by the facts that sorption was higher than the percentages of cationic species (for example, $\sim$99% of the applied fluoroquinolones were sorbed to the LVef whereas only 19% of these molecules were cationic) and that K_d values were correlated with exchangeable calcium contents of the soils ($r = 0.69–0.78$, $p < 0.01$).

Table 3
Sorption coefficients (K_d, L kg^{-1}) for the fluoroquinolones and sulfonamides in the studied soils.

Soils	Fluoroquinolones[a]				Sulfonamides[b]				
	NOR	CIP	DAN	ENR	SDZ	SMX	SCP	SDI	STA
	K_d (L kg^{-1})								
LVA1	5852.3 H	2878.8 F	2834.5 I	2127.7 H	1.2 H	1.1 G	1.6 H	1.3 KL	1.6 G
LVef	168 860.8 F	11 387.9 DE	17 194.1 F	9904.5 F	5.7 D	3.8 E	6.1 EF	13.2 E	25.7 C
PVA1	999.9 J	726.8 H	847.7 K	544.2 I	0.8 J	0.7 H	0.7 J	1.0 L	1.0 I
PVA5	36 209.1 D	40 608.0 C	50 860.3 C	53 654.0 C	10.9 C	8.2 C	5.3 GF	22.1 C	67.1 A
RQ	1499.1 I	1102.7 G	1249.6 J	779.7 I	1.1 HI	1.0 G	1.1 I	1.4 K	1.3 H
RL	34 865.4 D	41 125.8 C	30 097.6 DE	37 184.5 C	3.2 E	3.7 E	7.0 DE	4.7 H	8.8 E
NX	10 418.6 G	9658.4 E	9929.8 G	12 324.3 EF	4.6 D	5.4 E	8.2 D	7.7 F	19.4 D
Nvef	156 926.9 B	261 147.1 B	127 466.3 B	124 880.6 B	14.3 A	14.6 B	41.9 B	32.0 A	62.5 AB
GM	48 867.5 C	45 443.2 C	31 717.2 D	24 806.0 D	12.7 A	28.5 A	70.1 A	26.4 B	55.5 B
CX	26 088.8 E	11 952.1 DE	10 826.0 G	12 511.7 EF	1.3 G	2.7 F	4.6 G	2.6 I	4.3 F
SX	20 927.5 EF	16 019.8 D	23 584.4 E	14 490.1 E	3.1 F	3.8 E	6.7 E	5.9 G	7.7 E
TC	9035.2 G	3515.1 F	4947.4 H	4160.0 G	0.9 IJ	1.1 G	1.3 I	1.8 J	1.3 H
MT	335 633.6 A	1 277 873.9 A	255 643.7 A	251 430.0 A	7.8 B	7.4 D	13.3 C	16.3 D	28.1 C
Mean	54 168.1	132 572.3	43 630.7	42 215.2	5.2	6.3	12.9	10.5	21.9
Median	20 927.5	11 952.1	17 194.1	12 511.7	3.2	3.8	6.1	5.9	8.8

Different capital letters in the same column represent different mean K_d values according Tuckey test ($p < 0.05$).
[a] NOR = norfloxacin, CIP = coiprofloxacin, DAN = danofloxacin, ENR = enrofloxacin.
[b] SDZ = sulfadiazine, SMX = sulfamethoxazole, SCP = sulfachloropyridazine, SDI = sulfadimidine, and STA = sulfathiazole.

The lack of correlation between soil organic carbon or Al and Fe oxide contents on the one hand and K_d values on the other excludes hydrophobic partitioning and surface complexation as important mechanisms of fluoroquinolone sorption under tropical conditions, as proposed by Vasudevan et al. (2009). Soil organic matter was positively correlated with CEC_t ($r = 0.74$, $p < 0.01$), but not with CEC_e ($r = 0.22$), highlighting its major importance as a reservoir of negative charges under tropical conditions. As a matter of fact, organic matter can contribute up to 95% of total CEC in tropical environments, mainly in highly weathered soils having less reactive minerals, such as the Ultisols and Oxisols that encompass about 60% of Brazilian territory (Soares and Alleoni, 2008). A lack of correlation between soil organic carbon and sorption is common for compounds that have pH-dependent speciation (various pK_a values), such as the fluoroquinolones, with mechanisms other than hydrophobic partitioning dictating the mechanism of sorption (Vasudevan et al., 2009).

Figueroa-Diva et al. (2010) found that the sorption of fluoroquinolones (NOR, CIP, and ENR) was affected mainly by soil CEC, and reported little effect from soil oxide or organic carbon contents. Vasudevan et al. (2009) also found cation exchange to be a dominant process explaining ciprofloxacin sorption to soils, but reported that the influence of soil organic carbon content was unclear. They also observed that soil metal oxide contents played an important role, especially at higher pH values (>5.5). Under those conditions, they speculated that positively charged sites in the oxide surfaces may strongly interact with the carboxyl group of the fluoroquinolones (Gu and Karthikeyan, 2005; Vasudevan et al., 2009).

3.2. Sulfonamide sorption

K_d values for sulfonamides were highly variable among soils, ranging from 0.7 to 70.1 L kg^{-1} (Table 3). These values correspond to 24.6% and 96.9% of the amounts applied, respectively, meaning that sorption of sulfonamides varied from low to high potential depending on soil properties. Mean K_d values ranged from 5.2 to 21.9 L kg^{-1} and median K_d values ranged from 3.2 to 8.8 L kg^{-1} (Table 3), indicating that sorption was low in most soils. The median values were within the range of those reported elsewhere (0.6–7.4 L kg^{-1}, Sarmah et al., 2006), but the maximum K_d values (14.3, 28.5, 70.1, 32.0, and 62.5 L kg^{-1} for SDZ, SMX, SCP, SDI, and STA, respectively) were higher.

All the sulfonamides studied will tend to leach ($K_d < 5.0$ L kg^{-1}) from soils with high sand (>70%), low OC (<1.5%), and low CEC_t (<15 mmol$_c$ dm^{-3}) contents (Tables 2 and 3), such as the LVA1, PVA1, RQ, and TC soils. Most will also tend to leach from the RL, CX, and SX soils (sand = 45–66%, OC = 2.0–3.0%, and CEC_t = 35–45 mmol$_c$ dm^{-3}) (Table 3). By contrast, none of these compounds will tend to leach from soils with high OC (>4.0%) and clay (>35%) contents and relatively high CEC_t (>80 mmol$_c$ dm^{-3}, considering tropical soils), such as the PVA5, NVef, GM, and MT soils (Table 3). Indeed, K_d values were positively correlated with CEC_t ($r = 0.87$–0.90, $p < 0.01$) and clay content ($r = 0.76$–0.86, $p < 0.01$) and negatively correlated with sand content ($r = -0.85$ to -0.97, $p < 0.01$) of the soils (Table 4). In addition, sorption of the sulfonamides, in contrast to the fluoroquinolones, was also correlated with soil OC content ($r = 0.67$–0.78, $p < 0.01$) (Table 4). This correlation was much improved by removing the PVA5 and NVef soils ($r = 0.93$–0.96, $p < 0.01$), likely because they differ in terms of clay mineralogy (the PVA5 has illite and hydroxy-interlayer-vermiculate plus the usual kaolinite) and iron and aluminum oxide contents (very high in the NVef) (Table 2), which may have contributed to their enhanced sorption (Table 3). This highlights the fact that clay minerals are also an important factor influencing sulfonamide sorption. Nevertheless, it should be noted that OC, clay, and CEC_t were highly correlated among themselves ($r = 0.74$ for OC $\times$ CEC_t, $p < 0.01$; 0.79 for clay $\times$ CEC_t, $p < 0.01$; and 0.64 for clay $\times$ OC, $p < 0.05$).

The literature suggests that sulfamethazine sorption is influenced mainly by soil OC, but also by soil pH (Lertpaitoonpan et al., 2009). For sulfathiazole, sorption was an order of magnitude higher in organic than in inorganic sorbents, such as clay minerals, suggesting that OC plays a major role in the sorption of sulfonamides to soils and sediments (Kahle and Stamm, 2007). Sukul et al. (2008) also found high variation in the K_d values of sulfadiazine in five soils (from 0.1 to 24.3 L kg^{-1}) and reported that sorption correlated well with the organic carbon content of the soils. Thiele-Bruhn et al. (2004) concluded that the sorption of sulfonamides was influenced by their molecular structure and physicochemical properties; the presence of accessible functional groups at organic-mineral surfaces; and the accessibility of voids and cavities in the three-dimensional structure of soil organic matter and

Table 4
Correlation coefficients (r) between K_d values and descriptors of soil attributes[a] for the studied fluoroquinolones and sulfonamides.

	pH-$CaCl_2$	Ca	Mg	K	Al	H + Al	OC	Sand	Clay	CEC_e	CEC_t	FeDCB	FeAO	AlAO
Fluoroquinolones[b]														
NOR	0.26 NS	0.69**	0.54 NS	0.55 NS	0.12 NS	0.42 NS	0.44 NS	−0.80**	0.70**	0.72**	0.79**	0.51 NS	0.46 NS	0.51 NS
CIP	0.31 NS	0.78**	0.59*	0.53 NS	0.05 NS	0.39 NS	0.41 NS	−0.80**	0.71**	0.79**	0.84**	0.53 NS	0.47 NS	0.53 NS
DAN	0.39 NS	0.76**	0.64*	0.62*	0.02 NS	0.36 NS	0.43 NS	−0.86**	0.73**	0.80**	0.81**	0.55*	0.507 NS	0.56*
ENR	0.35 NS	0.77**	0.61*	0.58*	0.02 NS	0.35 NS	0.39 NS	−0.83**	0.69**	0.83**	0.80**	0.52 NS	0.47 NS	0.52 NS
Sulfonamides[c]														
SDZ	0.36 NS	0.66*	0.62*	0.64*	0.19 NS	0.53 NS	0.71**	−0.94**	0.84**	0.72**	0.89**	0.57*	0.55 NS	0.60*
SMX	0.23 NS	0.52 NS	0.50 NS	0.53 NS	0.42 NS	0.72**	0.78**	−0.89**	0.76**	0.67*	0.90**	0.44 NS	0.427 NS	0.48 NS
SCP	0.15 NS	0.45 NS	0.45 NS	0.48 NS	0.45 NS	0.74**	0.78**	−0.85**	0.76**	0.55 NS	0.87**	0.46 NS	0.46 NS	0.51 NS
SDI	0.49 NS	0.67*	0.69**	0.74**	0.19 NS	0.52 NS	0.68**	−0.98**	0.86**	0.70**	0.89**	0.62*	0.61*	0.65*
STA	0.49 NS	0.68*	0.71**	0.73**	0.19 NS	0.49 NS	0.67*	−0.96**	0.85**	0.74**	0.88**	0.60*	0.59*	0.63*

NS = not significant.
[a] H + Al = potencial acidity; OC = organic carbon; CEC_e = effective cation exchange capacity; CEC_t = total cation exchange capacity; FeDCB = iron extracted by sodium dithionite-citrate-bicarbonate solution; and FeAO and AlAO = iron and aluminium oxides extracted by acid ammonium oxalate solution.
[b] NOR = norfloxacin, CIP = coiprofloxacin, DAN = danofloxacin, ENR = enrofloxacin.
[c] SDZ = sulfadiazine, SMX = sulfamethoxazole, SCP = sulfachloropyridazine, SDI = sulfadimidine, and STA = sulfathiazole.
* = significant at $p < 0.05$.
** = significant at $p < 0.01$ according T-test.

its combination with the mineral matrix forming organic-mineral complexes, conditions directly linked to the quantity and quality of soil organic matter. Figueroa-Diva et al. (2010) found that K_d values were sensitive to the R-substituent on the sulfonamide structure and that K_d followed predictions based on compound hydrophobicity ($\log K_{ow}$), supporting the hypothesis that sorption is governed by hydrophobic partition. Although we could not identify a clear relationship between our K_d values and the $\log K_{ow}$ of the molecules (Table 1) or the molecular surface area as found for clay minerals by Gao and Pedersen (2005), sulfadiazine had the lowest sorption, which is coherent with its lowest $\log K_{ow}$ value. We were also unable to predict sorption order (SDZ < SMX < SDI < SCP < STA, Table 3) based on the mass fraction of neutral species, which corresponded to mean values of 90%, 79%, 99%, 83%, and 96%, respectively. These findings support the hypothesis that sorption of sulfonamides is not only governed by hydrophobic partition in highly weathered soils, such as those in Brazil.

Gao and Pedersen (2010) showed that on a mass basis organic matter has a higher affinity for neutral sulfonamide antimicrobials than smectites, but due to their relative amounts both are likely to contribute to overall sorption. In a previous study, they found that sulfamethazine sorption to kaolinite was nearly invariant over a broad range of proton activities (pH 4.3–7.0), suggesting little interaction of neutral species with surfaces exhibiting variable charges (i.e., edge surfaces) (Gao and Pedersen, 2005). In the case of neutral species, surface-area-normalized K_d values for kaolinite exceeded those for montmorillonite, suggesting that lower permanent negative charge density on kaolinite siloxane surfaces provided larger domains for their sorption (Gao and Pedersen, 2005). Essington et al. (2010) observed that sulfadimidine sorption to kaolinite far exceeded that to montimorillonite and that sorption coefficients were greatest in the most acidic systems, meaning that cation exchange processes prevailed under those conditions.

No correlations were observed between soil pH and K_d values (r = 0.15–0.49, $p > 0.05$), even when K_d was normalized to OC (K_{oc}) or CEC (K_{CEC}) values (data not shown). Nevertheless, it is commonly postulated that sulfonamide sorption decreases as pH increases due to molecule speciation (ionization), which implies that anionic species sorb less than neutral species, which sorb less than cationic species due to electrostatic interactions between the ionogenic species and the soil particles and to hydrophobic partitioning of the neutral species to the organic fraction of the soil (Lertpaitoonpan et al., 2009; Biatk-Bielińska et al., 2012). Sulfonamides are amphoteric compounds with two relevant ionizable groups, the basic 4-amine aromatic (pK_{a1} = 1.6–2.6) and the acid sulfonamide (pK_{a2} = 5.7–8.0) moieties (Table 1) (Ikehata et al., 2006). However, only the dissociation constant of the acid group (pK_{a2}) is relevant for our set of soils, which have pH values ranging from 4.3 to 6.9. Under these pH conditions (with the exception of the LVef soil (pH = 6.9)), most molecules were neutral. This explains the lack of correlation with pH, because their sorption is governed mostly by hydrophobic partitioning (Sukul et al., 2008). The fact that variable charge edges of kaolinite, which are pH-dependent and very abundant in our soils, do not contribute substantially to the overall sorption of sulfonamides (Gao and Pedersen, 2005) may also corroborate this explanation.

In this study it was not possible to establish a model to predict sorption based on the individual magnitude of sorption of the different species and by normalizing K_d to the soil property that most affected sorption (in this case CEC), as has been done for other ionogenic organic compounds (Jafvert, 1990; Fontaine et al., 1991; Uslu et al., 2008; Sassman and Lee, 2005; Gao and Pedersen, 2005). These models seem not to hold for highly weathered soils having high Fe and Al oxyhydroxide contents and mostly kaolinite and gibbsite in the clay fraction (Regitano et al., 2005; Sassman and Lee, 2005; Gao and Pedersen, 2005). This supports the notion that sorption of sulfonamides to these soils may also be influenced by non-hydrophobic interactions with organic or mineral surfaces. The oxyhydroxides (mainly hematite and gibbsite) and kaolinite have already been implicated in the sorption of other ionogenic organic molecules having acid behavior (Huang et al., 1977; Goetz et al., 1986; Regitano et al., 1997; Gao and Pedersen, 2005). Unfortunately, most published research on sorption of sulfonamides focuses exclusively a small set of soils (three to five), having low Fe and Al oxyhydroxide contents and different pH values (usually higher than 5.5 or lower than 4.0) that preclude comparisons with our soils.

4. Conclusion

Sorption of fluoroquinolones and sulfonamides was greatly affected by soil attributes. Fluoroquinolone sorption was high ($K_d \geqslant 544$ L kg^{-1}) even in worst-case scenarios (sand $\geqslant$840 g kg^{-1}, OC $\leqslant$9.6 g kg^{-1}, and $CEC_t \leqslant$32 $mmol_c$ dm^{-3}) whereas sulfonamide sorption varied as much as 100 times among soils (K_d = 0.7–70.1 L kg^{-1}), reflecting variation in leaching potential. Soil texture and total cation exchange capacity were the soil attributes that most strongly influenced sorption, while a direct effect of soil pH and/or Fe and Al oxide contents on sorption was not observed. OC was only correlated with sulfonamide sorption. For the fluoroquinolones, cation exchange appeared to be the dominant sorption mechanism, although cation bridging and ion pairing could not be ruled out. For the sulfonamides, hydrophobic partition appeared to be important, but sorption was also affected by non-hydrophobic interactions with organic and/or mineral surfaces, mainly the Al and Fe oxides and hydroxides that are abundant in tropical soils.

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