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Occurrence and sorption of fluoroquinolones in poultry litters and soils from São Paulo State, Brazil

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ABSTRACT

Animal production is one of the most expressive sectors of Brazilian agro-economy. Although antibiotics are routinely used in this activity, their occurrence, fate, and potential impacts to the local environment are largely unknown. This research evaluated sorption–desorption and occurrence of four commonly used fluoroquinolones (norfloxacin, ciprofloxacin, danofloxacin, and enrofloxacin) in poultry litter and soil samples from São Paulo State, Brazil. The sorption–desorption studies involved batch equilibration technique and followed the OECD guideline for pesticides. All compounds were analyzed by HPLC, using fluorescence detector. Fluoroquinolones' sorption potential to the poultry litters ($K_d \leq 65$ L kg^{-1}) was lower than to the soil (K_d ~40,000 L kg^{-1}), but was always high (≥69% of applied amount) indicating a higher specificity of fluoroquinolones interaction with soils. The addition of poultry litter (5%) to the soil had not affected sorption or desorption of these compounds. Desorption was negligible in the soil (≤0.5% of sorbed amount), but not in the poultry litters (up to 42% of sorbed amount). Fluoroquinolones' mean concentrations found in the poultry litters (1.37 to 6.68 mg kg^{-1}) and soils (22.93 μg kg^{-1}) were compatible to those found elsewhere (Austria, China, and Turkey). Enrofloxacin was the most often detected compound (30% of poultry litters and 27% of soils) at the highest mean concentrations (6.68 mg kg^{-1} for poultry litters and 22.93 μg kg^{-1} for soils). These results show that antibiotics are routinely used in poultry production and might represent one potential source of pollution to the environment that has been largely ignored and should be further investigated in Brazil.

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1. Introduction

Brazil is a worldwide leader in the production and exportation of animal products, such as poultry and cattle meat (USDA — United States Department Of Agriculture, 2011). Massive quantities of antibiotics agents are used in local animal production units, but we are unaware of any official statistics on the amounts used and sold in the country. Several overseas studies reported the occurrence of veterinary antibiotic residues in animal manures (typically in mg kg^{-1}) (Martínez-Carballo et al., 2007; Xian-Gang et al., 2008; Zhao et al., 2010) and also in manure fertilized agricultural soils (typically in μg kg^{-1}) (Karci and Balcioğlu, 2009; Uslu et al., 2008). These residues may negatively affect the environment, mainly through chronic toxic effects to terrestrial organisms or due to the controversial but worrisome potential influence on microorganism's resistance (Kemper, 2008).

The fluoroquinolones are one of the most used class of compounds for veterinary purposes in the world (Picó and Andreu, 2007) and have limited metabolism in the animal body (20–80%) (Boxall et al., 2004). In addition, they are strongly sorbed (K_d = 260 to 5012 L kg^{-1}, Sarmah et al., 2006) and slowly degradable ($t_{1/2}$ ~1000 days in biosolid amended soils, Walters et al., 2010) compounds. Soil fertilization with contaminated animal manure resulted in continuous soil accumulation of these residues (Picó and Andreu, 2007). Concentrations as high as 225 and 1420 mg kg^{-1} of norfloxacin and enrofloxacin, respectively, were found in chicken manures from China (Zhao et al., 2010), whereas 20 to 50 μg kg^{-1} of enrofloxacin were found in Turkish soils sampled seven months after they were fertilized with contaminated manure (Karci and Balcioğlu, 2009).

The fluoroquinolones are amphoteric compounds with two relevant ionizable functional groups, the 3-carboxyl group (pK_a ~6) and the N-4 in the piperazine substituent (pK_a ~8), which makes their sorption a pH-dependent process (Picó and Andreu, 2007). Sorption to solid matrices is one of the main mechanisms of fluoroquinolone dissipation in the environment. Concentrations as high as 2 mg kg^{-1} of norfloxacin and ciprofloxacin in raw sewage sludge (Golet et al., 2003) and 1.56 mg kg^{-1} of ofloxacin in river sediments (Yang et al., 2010) were reported. The polar nature and the high sorption potential of the fluoroquinolones suggest that mechanisms other

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than hydrophobic partitioning play an important role on their sorption (Uslu et al., 2008).

A good understanding of antibiotic concentration in the environment as well as the main mechanisms responsible for their retention is a crucial aspect for an appropriate evaluation of potential microbial exposure and all the associated risks these contaminants may represent to other organisms and also to human health (Vasudevan et al., 2009). Almost all of the currently available data were acquired under temperate conditions, while very little is known about the dynamics and impacts of major veterinary antibiotics in tropical environments, such as in Brazil, where climatic conditions and soil types are very distinct, as well as poultry farm management and manure application, among others.

This research evaluated the sorption–desorption potential of three fluoroquinolone antibiotics (norfloxacin, ciprofloxacin, and enrofloxacin) to two poultry litter types (rice straw and pine dust), as well as the effect of poultry litter addition (rice straw) on the sorption–desorption of these compounds to a typical Brazilian soil. It also provided natural environmental concentrations of norfloxacin, ciprofloxacin, danofloxacin, and enrofloxacin in poultry litters and soils collected at different production areas of São Paulo State, Brazil.

2. Materials and methods

2.1. Reagents and standards

Norfloxacin (NOR), ciprofloxacin (CIP), danofloxacin (DAN), and enrofloxacin (ENR) were purchased from Sigma-Aldrich, with purity higher than 98%. The stock standard solutions (1.0 mg mL^{-1}) were prepared in methanol containing 1% of acetic acid, stored at −18 °C in the dark, and used within 90 days. Ultra-pure water was used in order to prepare all aqueous solutions. Magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$), ammonium hydroxide (NH_4OH), calcium chloride ($CaCl_2$), and oxalic acid ($C_2H_2O_4 \cdot 2H_2O$) were all analytical grade. The organic solvents used (methanol and acetonitrile) were all HPLC grade.

2.2. Animal manure and agricultural soil samples

Two poultry litters from poultry houses already containing rice straw and pine dust as substrates and a typical Brazilian soil (Typic Haplustox) were selected for the sorption–desorption studies. Their main physicochemical properties are presented in Table 1.

In order to determine fluoroquinolone environmental concentrations, 46 poultry litters and 11 soils (0–20 cm) were collected from different producing regions of São Paulo State, Brazil. All soils had a history of poultry litter application. Each sample (~500 g of either poultry litter or soil) was attained by homogeneously mixing 12 subsamples randomly collected inside a poultry house or an homogeneous agricultural field, respectively. After collection, the samples were placed into plastic bags and transported under refrigerated conditions within the same day. The samples were homogenized, sieved, lyophilized within 48 h, and analyzed within a week after collection (stored at −18 °C until extraction).

2.3. Extraction procedures

Fluoroquinolones' extraction was based on the method proposed by Turiel et al. (2006). However, a centrifugation step (10 min, 3560 g) was added after the ultrasonic bath, as proposed by Karci and Balcioğlu (2009). Briefly, 1 g of either the soil or the poultry litter and 8 mL of an aqueous solution of $Mg(NO_3)_2$ (29% w/v, adjusted to pH 8.1 with 4% of ammonia) were placed into Teflon tubes (50 mL), mixed in a vortex for 60 s, and let in ultrasonic bath for 30 min at room temperature. Samples were then centrifuged and the supernatants were filtered (0.45 μm syringe filter) prior to HPLC analysis. Samples were all analyzed in duplicate.

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 equal to 50 μL. An isocratic elution was used and the mobile phase was composed of 72% of oxalic acid 0.01 mol L^{-1} adjusted to pH 4.0 (solvent A) and 28% of methanol (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.

In order to built the calibration curves and to validate the method, triplicates of a residue-free poultry litter and soil were spiked with different concentrations of fluoroquinolones (50, 150, 500, 1000, 2000 and 4000 μg kg^{-1}) and kept in the dark overnight at room temperature for sample equilibration prior to extraction. The correlation coefficients were ≥0.99. The limits of quantification for all compounds ranged from 3.35 to 27.38 μg kg^{-1} for soil and from 78.12 to 208.10 μg kg^{-1} for poultry litter based on seven replicates of the matrix blank. The recovery tests were performed at three fortification levels (500, 1000 and 4000 μg kg^{-1}) and five replicates, and ranged from 68.6 to 108.6% (standard deviation ≤7%) for the soil and from 67.4 to 99.2% (standard deviation ≤15%) for the poultry litter.

2.5. Sorption and desorption

The batch experiments followed the OECD guideline for pesticides (OECD, 2000), with a pre-test performed to define solid:solution ratio (2 g:30 mL), equilibration period (24 h), compounds stability, and tube walls sorption. In all cases compound losses were lower than 5% (data not shown). When needed, the poultry litter (rice straw) was added to the soil according to fertilization recommendations (5% w/w). It was thoroughly mixed (15 min) prior the addition of antibiotic solutions. Triplicates of 2 g of the samples (poultry litter, soil or soil amended with poultry litter) and 30 mL of the fluoroquinolone (NOR, CIP and ENR) solutions at different concentrations (170; 340;

Table 1
Characterization of poultry litters and a typical Brazilian soil used in the sorption studies.

Sample	pH-$CaCl_2$	CEC	Sand	Clay	Silt	OC	TN	P	K	Ca	Mg
		mmol$_c$ dm^{-3}	g kg^{-1}			%		g kg^{-1}			
Poultry litter (rice straw)	7.4	–	–	–	–	39.90	4.19	32.40	32.90	31.90	4.60
Poultry litter (pine dust)	7.1	–	–	–	–	37.09	4.50	20.30	23.90	21.40	3.80
Soil	5.9	127.8	122	754	116	1.62	–	0.02	0.12	0.56	0.32

OC = organic carbon content; TN = total nitrogen.

680; 1360; and 2720 μg L^{-1} prepared in 0.01 mol L^{-1} $CaCl_2$) were added to Teflon tubes (50 mL), horizontally shaken at 200 rpm for 24 h, and then centrifuged at 3560 *g* for 10 min. The supernatants were filtered (0.22 or 0.45 μm) and the equilibrium concentration (C_e) were determined by HPLC as described above, but with slight modifications (flow rate = 0.8 mL min^{-1} and mobile phase = 78% of formic acid 0.1% in aqueous solution and 22% of acetonitrile). The amount of antibiotic sorbed (S) was calculated by the difference between initial (C_i) and equilibrium concentrations, taking into account the solid:solution ratio. The data were then fitted to the Freündlich equation ($S = K_f C_e^N$) and to its linear form ($S = K_d C_e$) in order to estimate the mean partition coefficients (K_d^{mean} = average of K_d values attained at individual concentrations).

Desorption was evaluated at two concentrations (680 and 2720 ng mL^{-1}), in 4 steps of 24 h (totalizing 96 h). For each step, an aliquot of 20 mL of the supernatant was taken and replaced by a fresh 0.01 mol L^{-1} $CaCl_2$ solution, shaken for 24 h, centrifuged at 3560 *g* for 10 min, and the supernatant concentrations were determined as described above. All samples were previously tested to guarantee that they were not contaminated with fluoroquinolones.

3. Results and discussion

3.1. Sorption and desorption

Sorption potential of fluoroquinolones to the poultry litters (K_d ranged from 34 to 65 L kg^{-1}) was much lower than to the soil (K_d ranged from 40,656 to 40,783 L kg^{-1}), but still was high with at least 69% of the applied amount sorbed (Table 2). In addition, the poultry litter type (rice straw or pine dust) had little effect on fluoroquinolones' sorption potential, but ciprofloxacin showed the lowest (K_d = 34 to 36 L kg^{-1}) whereas norfloxacin had the highest (K_d = 53 to 65 L kg^{-1}) sorption potential to these substrates (Table 2). Hysteresis was very pronounced in both poultry litters (Figs. 1, 2 and 3) suggesting low desorption potential for fluoroquinolones (<26% of the sorbed amount, Table 2), except for norfloxacin and ciprofloxacin in the rice straw poultry litter at the highest concentration (2720 ng mL^{-1}), in which 40 and 42% of the sorbed amounts were respectively desorbed (Table 2).

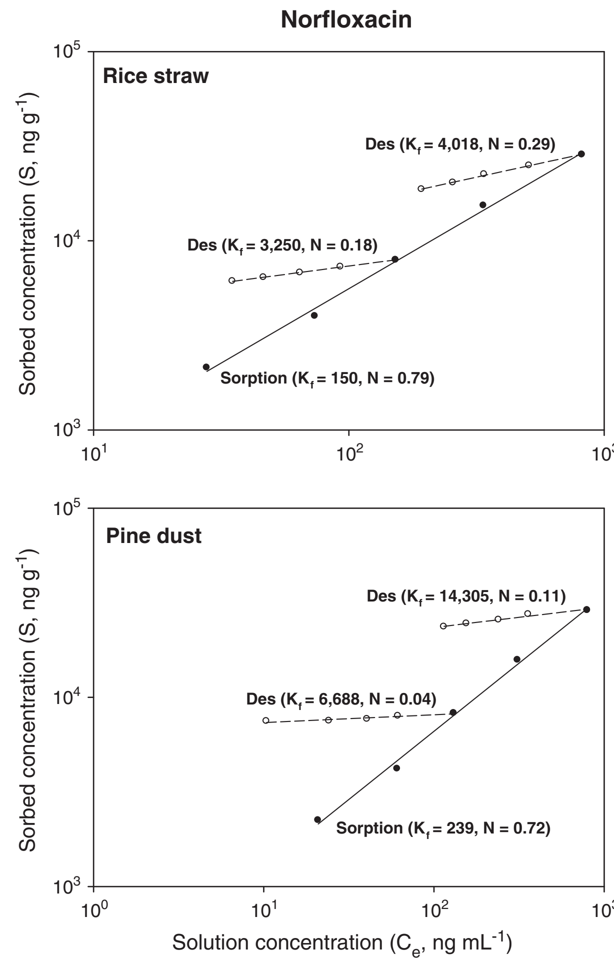

Fig. 1. Sorption–desorption of norfloxacin in poultry litters (rice straw and pine dust). K_f = Freündlich sorption coefficient and N = exponential coefficient.

Table 2
Parameters of fluoroquinolones' sorption and desorption in poultry litters, soil and soil with poultry litter addition.

Parameters	NOR	CIP	ENR
	Poultry litter (rice straw)		
Average K_d (L kg^{-1})	52.6 ± 15.4	36.3 ± 3.2	49.0 ± 4.1
Amount sorbed (% of applied)	76.9 ± 5.0	70.7 ± 1.8	76.5 ± 1.6
K_f ($g^{1-N} L^N kg^{-1}$)	150	43	33
N	0.79	0.97	1.08
Desorption at 680 ng mL^{-1} (% of sorbed)	25.0	25.1	24.3
Desorption at 2720 ng mL^{-1} (% of sorbed)	40.1	42.3	25.9
	Poultry litter (pine dust)		
Average K_d (L kg^{-1})	65.1 ± 26.5	34.1 ± 3.4	38.0 ± 7.8
Amount sorbed (% of applied)	79.7 ± 6.3	69.3 ± 2.0	71.1 ± 5.0
K_f ($g^{1-N} L^N kg^{-1}$)	239	44	16
N	0.72	0.95	1.16
Desorption at 680 ng mL^{-1} (% of sorbed)	9.6	18.7	20.5
Desorption at 2720 ng mL^{-1} (% of sorbed)	19.7	27.7	20.1
	Soil (Typic Haplustox)		
K_d at 2720 ng mL^{-1}(L kg^{-1})	40,772	40,783	40,656
Sorption at 2720 ng mL^{-1} (% of applied)	99.9	100.0	99.6
Desorption at 2720 ng mL^{-1} (% of sorbed)	nd[a]	0.22	nd
	Soil plus rice straw poultry litter (5%)		
K_d at 2720 ng mL^{-1}(L kg^{-1})	40,716	40,728	40,595
Sorption at 2720 ng mL^{-1} (% of applied)	99.8	99.8	99.5
Desorption at 2720 ng mL^{-1} (% of sorbed)	0.05	0.04	0.46

NOR = norfloxacin; CIP = ciprofloxacin; ENR = enrofloxacin.
K_d = average sorption coefficient.
K_f = Freündlich sorption coefficient.
N = exponential coefficient of the Freündlich equation.
[a] nd = not detected.

The lower affinity of fluoroquinolones to the poultry litters than to the soil might be related to their smaller amount of sorption sites available as well as to their slightly alkaline pH values (Table 1). Despite the much higher organic carbon content (OC) of the poultry litters (Table 1), the reactivity of their functional groups should be limited, thus offering fewer exchange sites for sorption. Moreover, fluoroquinolones' sorption tends to be lower at higher pH values due to the dominium of either the neutral or the anionic species (Vasudevan et al., 2009). Nonetheless, sulfonamide antibiotics showed stronger sorption to acid pig slurry (pH 4.8) than to soil (Thiele-Bruhn and Aust, 2004). The carboxylic and phenolic moieties from the particulate matter of the manure were assumed to provide exchange sites, increasing sorption affinity.

Sorption of all compounds to soil was very high (K_d ranged from 40,656 to 40,783 L kg^{-1}, totalizing almost 100% of applied amount) whereas desorption was negligible (always <0.5% of the sorbed amount) (Table 2), which suggests strong specific interactions between the fluoroquinolone molecules and the soil particles. This is ratified by the fact that sorption quantification was only possible at the highest concentration. The sorption of norfloxacin, ciprofloxacin, and ofloxacin was also fast (less than 24 h) and high (K_f ranged from 7943 to 12,309 $\mu g^{1-1/n} (cm^3)^{1/n} g^{-1}$) in a wetland soil receiving wastewater, with most of the applied amount being sorbed (Conkle et al., 2010). The authors credited sorption as the major mechanism responsible for

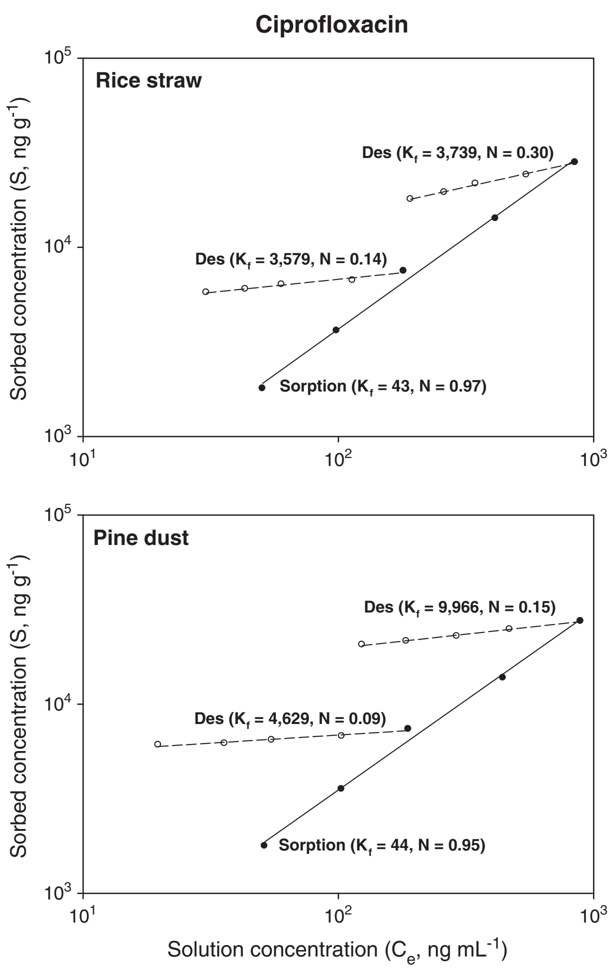

Fig. 2. Sorption–desorption of ciprofloxacin in poultry litters (rice straw and pine dust). K_f = Freündlich sorption coefficient and N = exponential coefficient.

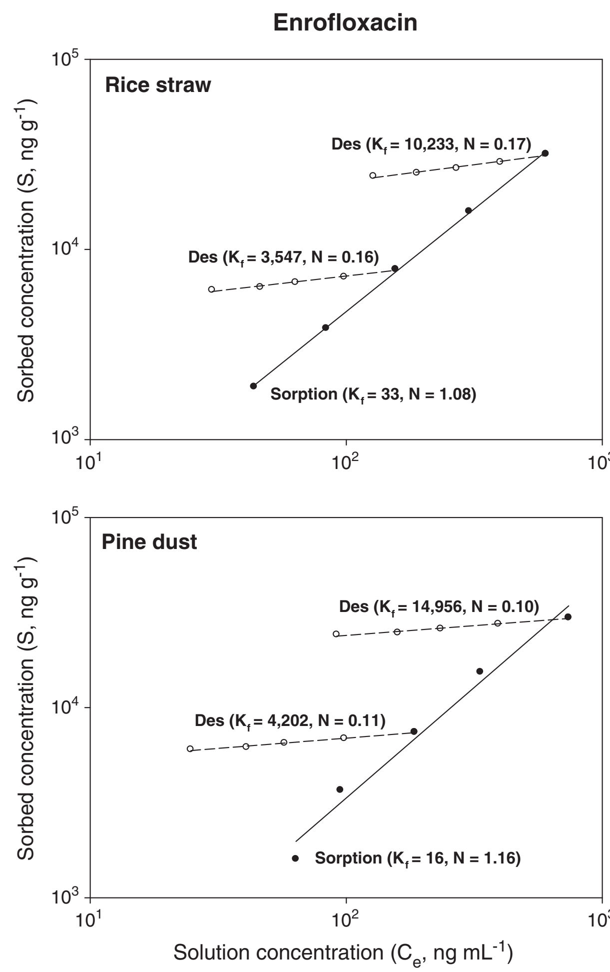

Fig. 3. Sorption–desorption of enrofloxacin in poultry litters (rice straw and pine dust). K_f = Freündlich sorption coefficient and N = exponential coefficient.

removal of these antibiotics from wastewater. Another work showed that cation exchangeable capacity was the main soil attribute affecting ciprofloxacin sorption to soils, with soil metal oxide content playing a secondary but also important role particularly at higher pH values (≥5.5) (Vasudevan et al., 2009). The contribution of soil OC content to sorption was unclear, but mechanisms such as cation exchange, cation bridging, and surface complexation contributed to the net ciprofloxacin sorption to soils (Vasudevan et al., 2009). For another antibiotic class, the sulfonamides, sorption was influenced by the molecular structures and physicochemical properties of the compounds, the presence of accessible functional groups at organomineral surfaces, and the accessibility of voids and cavities in the three-dimensional structure of soil organic matter and its combination with the mineral matrix forming organomineral complexes (Thiele-Bruhn et al., 2004).

Fluoroquinolones bind to clay minerals via several mechanisms, such as cation bridging, electrostatic interactions, and H-bonding (Speltini et al., 2011), and to humic substances mainly via multiple H-bonding through the polar groups (Aristilde and Sposito, 2010). The soil adopted is highly weathered and has low activity clays (mostly kaolinite), high Fe and Al oxide contents, low organic matter content, low CEC, and pH-dependent charges (Table 1) (Fontes and Alleoni, 2006), occupying as much as 38% of the Brazilian territory (Regitano and Leal, 2010). Therefore, it seems reasonable to hypothesize that surface complexation to the soil oxides, mainly Fe and Al, played an important role as a mechanism for fluoroquinolones' sorption. Strong interactions were also observed between ciprofloxacin and Fe and Al hydrous oxides, in particular with Fe oxides (K_d = 2072 L kg^{-1} at pH 6.5) (Gu and Karthikeyan, 2005). At this pH value, which is close to our soil (pH = 5.9), zwitterionic ciprofloxacin predominates and sorption was attributed mainly to the formation of a mononuclear bidentate complex between the Fe atoms and the carboxylate group of ciprofloxacin (Gu and Karthikeyan, 2005).

Addition of the rice straw poultry litter to the soil (5% w/w) had very little effect on the fluoroquinolones' sorption. The K_d values ranged from 40,595 to 40,783 L kg^{-1} (Table 2). Nevertheless, manure or slurry addition to soils may affect sorption since it changes their pH and organic matter nature (Boxall, 2008). As examples, sulfadiazine sorption was higher and desorption was lower when soil was amended with 4% of an alkaline pig slurry (pH of 7.6) (Sukul et al., 2008), whereas sulfachloropyridazine sorption was lower after the addition of an alkaline pig manure (Boxall et al., 2002). Thiele-Bruhn and Aust (2004) also found lower sorption coefficients for sulfonamides after addition of pig slurry to the soil, which was associated with the mobilizing effect of the dissolved organic matter present in the manure rather than with pH alterations. In this case, the competitive adsorption between dissolved organic matter and sulfonamide molecules and/or the binding of organic matter to soil minerals was the main mechanism through which pig slurry precluded sulfonamide sorption to the soil (Thiele-Bruhn and Aust, 2004).

3.2. Fluoroquinolones in poultry litters and soils

Three of the four studied fluoroquinolones (NOR, CIP and ENR) were detected in the poultry litters, but only enrofloxacin was detected in the

Table 3
Residual concentrations of fluoroquinolones in poultry litters and soils.

Compounds	Frequency (%)	Concentrations				
		Minimum	Maximum	Mean	Median	SD
Poultry litter (mg kg^{-1}), total of 46 samples						
NOR	6.5	0.80	4.55	2.55	2.30	1.89
CIP	4.3	0.65	2.13	1.37	1.37	1.08
DAN	0.0	nd[a]	nd	nd	nd	–
ENR	30.4	0.39	30.97	6.68	4.33	8.25
Soils (μg kg^{-1}), total of 11 samples						
NOR	0.0	nd	nd	nd	nd	–
CIP	0.0	nd	nd	nd	nd	–
DAN	0.0	nd	nd	nd	nd	–
ENR	27.0	17.36	26.69	22.93	24.7	4.89

NOR = norfloxacin; CIP = ciprofloxacin; DAN = danofloxacin; ENR = enrofloxacin.
SD = standard deviation.
[a] nd = not detected.

soils. Their concentrations were in the range of mg kg^{-1} in the poultry litters and in the range of μg kg^{-1} in the soils (Table 3). The mean values were comparable to those described elsewhere (Table 4). However, the maximum concentrations of norfloxacin, ciprofloxacin and enrofloxacin detected in poultry litters (4.55, 2.13, and 30.97 mg kg^{-1}, respectively) were much lower than those reported for the samples from different provinces of China (255.45, 45.59, and 1420.76 mg kg^{-1} for the same compounds; respectively) (Zhao et al., 2010). Danofloxacin was not detected, reflecting its low or even lack of use in São Paulo State, Brazil.

Enrofloxacin was found at the highest concentrations (mean = 6.68 mg kg^{-1} for the poultry litter and 22.93 μg $kg^{-1}$for the soil) and was the most often detected compound (30% of the poultry litter and 27% of the soil samples) (Table 3). In Austria, enrofloxacin was detected in 17% of the 30 animal manured soils at concentrations up to 370 μg kg^{-1}, in 25% of the chicken manures at concentrations up to 2.8 mg kg^{-1}, and in 38% of the turkey manures at concentrations up to 8.3 mg kg^{-1} (Martínez-Carballo et al., 2007). Their soil concentrations were higher than ours, but their manure concentrations were similar to ours. These researchers outlined soil contamination with fluoroquinolones, along with tetracyclines, as a critical result demanding further investigations with focus mainly on their ecotoxicology.

Our results showed that enrofloxacin is likely the most heavily used fluoroquinolone in poultry production areas of São Paulo State, Brazil. The low concentrations or the non-existence of fluoroquinolones in soils are due to one or more of the following reasons: (i) the soils were fertilized with uncontaminated poultry litters; (ii) the dilution factor after soil fertilization with poultry litter; (iii) the enhanced dissipation rate at tropical conditions due to the higher temperatures, precipitations, and biological activities; (iv) the high sorption potential at tropical conditions which reduces extraction efficiency over time; and (v) the intrinsic limitations of the analytical method, such as the established limit of quantification and the relative efficiency of the extraction method.

4. Conclusions

Sorption potential of fluoroquinolones was high in the poultry litters, but was much higher in a typical Brazilian soil. Addition of poultry litter (either rice straw or pine dust) did not affect these compounds' sorption to the soil. Soil desorption was negligible (<0.5%). A simple, fast, and efficient method could be used for fluoroquinolone quantification in poultry litters and soils. Fluoroquinolones' mean concentrations were compatible to those found in previous investigations performed overseas. Enrofloxacin was the compound most often detected, at higher concentrations, and uniquely found in soils.

This work embodies the first investigation on the occurrence of an important class of antibiotics used in Brazil and should serve as a basis for further studies. Nevertheless, it shows that fluoroquinolones

Table 4
Concentrations of fluoroquinolones in poultry litters and soils over the world.

	Country	NOR	CIP	DAN	ENR
		Poultry litters (mg kg^{-1})			
Martínez-Carballo et al. (2007)	Austria	na[a]	nd[a]	na	Up to 2.8
Xian-Gang et al. (2008)	China	na	0.3–3.0	na	na
Karci and Balcioğlu (2009)	Turkey	na	nd	na	0.06
Zhao et al. (2010)	China	Up to 225.5 (4.68)[b]	Up to 45.6 (3.78)	Up to 2.5 (0.72)	Up to 1420.8 (4.65)
		Soils (μg kg^{-1})			
Martínez-Carballo et al. (2007)	Austria	na	–	na	370
Uslu et al. (2008)	Turkey	na	53	na	13–204
Karci and Balcioğlu (2009)	Turkey	na	nd	na	50

NOR = norfloxacin; CIP = ciprofloxacin; DAN = danofloxacin; ENR = enrofloxacin.
[a] na = not analyzed; nd = not detected.
[b] Blanket values = geometric mean of the evaluated samples.

are routinely used in poultry production and represent a potential source of environmental pollution that has been largely ignored in the country up to now, deserving further attention given the importance of animal production to the country's economy.

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