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Sorption of norfloxacin in soils: Analytical method, kinetics and Freundlich isotherms

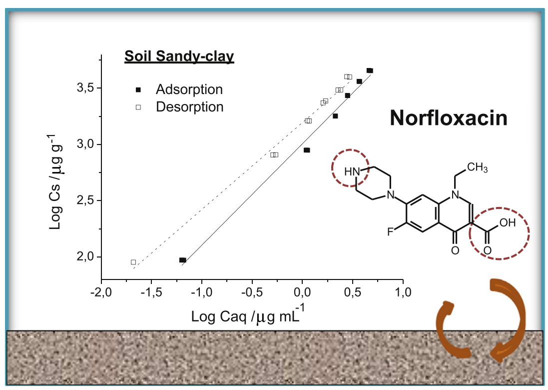
Livia Maniero Peruchi, Anne Hélène Fostier, Susanne Rath *

Institute of Chemistry, Department of Analytical Chemistry, University of Campinas, PO Box 6154, 13084-971 Campinas, SP, Brazil

HIGHLIGHTS

- The sorption of norfloxacin (NOR) was studied in four Brazilian soil–water systems.
- A strong matrix effect on chromatographic determination of NOR is present.
- The matrix effect is eliminated by the addition of EDTA.
- K_F values indicate that NOR is strongly sorbed on the evaluated soils.
- NOR is highly immobile in the evaluated soils.

GRAPHICAL ABSTRACT



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ABSTRACT

Fluoroquinolones are potent antibacterial agents that are active against a wide range of pathogenic organisms and are widely used in veterinary medicine. Fluoroquinolones and their metabolites may reach the soil through animal excreta or manure and may contaminate water and soils. The degree of sorption of these antimicrobials to soils varies widely, as does the mobility of these drugs. In the present study, sorption of norfloxacin in four soils of the state of São Paulo was investigated with batch equilibrium experiments. A strong matrix effect on the chromatographic determination of norfloxacin was verified. Sorption kinetics were best fit by a pseudo second-order model ($r > 0.99$), and sorption/desorption isotherms were well fit by the Freundlich model in log form ($r > 0.97$). Norfloxacin showed high affinity for soil particles, with K_F sorption values ranging from 643 to 2410 $\mu g^{1-1/n}(cm^3)^{1/n}g^{-1}$ and K_F desorption values ranging from 686 to 2468 $\mu g^{1-1/n}(cm^3)^{1/n}g^{-1}$. The high desorption K_F values indicate that norfloxacin is highly immobile in the evaluated soils.

1. Introduction

Veterinary drugs have contributed to great improvements in animal health and promoted increases in animal production, especially in management–intensive farming. Global sales of veterinary medicines were estimated at 20.1 billion dollars in 2010, of which Brazil was responsible for almost 10% (SINDAN, 2012).

Fluoroquinolones are among the most important classes of antibacterial agents used to treat a wide variety of diseases on intensive farms. Antibiotics, including fluoroquinolones, were banned as growth promoters in many countries due to bacterial resistance, and there is a global concern about the use of large amounts of antimicrobials in food animals.

* Corresponding author. Tel.: +55 19 3521 3084; fax: +55 19 3521 3023.
E-mail address: Susanne.rath@gmail.com (S. Rath).

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Norfloxacin (NOR) is a fluoroquinolone with high antibacterial activity against both Gram-negative and Gram-positive bacteria and is widely used in livestock and poultry production to prevent diseases (Sarmah et al., 2006). It is also used as a medication in aquacultures (Boxall et al., 2004). The presence of antimicrobials in the environment can have negative effects on aquatic and terrestrial systems, including toxic effects on biota, which may contribute to the development of antibiotic-resistant microorganism populations (Thiele-Bruhn, 2003; Sukul and Spiteller, 2007; Kemper, 2008; Brown and Balkwill, 2009; Speltini et al., 2011; Leal et al., 2012).

The occurrence of NOR and other fluoroquinolones in the environment has been widely studied and is attributed to several causes. Studies show that 50–68% of administered NOR is excreted in urine and feces as either the parent compound or its active metabolites. The application of contaminated animal manure or sewage as fertilizer can result in the direct release of NOR into soils. Concentrations as high as 225 mg kg^{-1} NOR were found in chicken manure samples in China (Zhao et al., 2010). Studies by Golet et al. (2003) showed the presence of fluoroquinolones, including NOR, in soil samples where sewage sludge had been applied (Golet et al., 2003).

Accumulation of fluoroquinolones in soil mostly depends on photostability, binding and sorption capabilities, persistence and leaching by water. These processes are, in turn, governed by pharmaceutical physicochemical properties, such as structure, size, shape, solubility, hydrophobicity, and speciation, and soil physical and chemical properties, such as organic matter content, texture, mineralogy, clay content, pH, ionic strength, and cation exchange capacity, as well as local weather conditions (Sarmah et al., 2006).

Norfloxacin is an amphoteric molecule with a structure consisting of a bicyclic aromatic ring skeleton with a carboxylic acid group ($pk_a = 6.30$) and a piperazinyl moiety ($pk_a = 8.38$), which makes its sorption on soil strongly pH-dependent (Zhang et al., 2012). Figueroa-Diva and coworkers suggest that the fluoroquinolone sorption potential is governed by the interaction of the fluoroquinolone base structure with soil, attributed mainly to soil cation exchange with little effect of soil oxide or organic carbon content (Figueroa-Diva et al., 2010). In addition, fluoroquinolones form stable complexes with several divalent and trivalent metal ions present in soil. Among these, Ca(II), Mg(II) and Al(III) complexes have the largest stability constants (Turiel et al., 2006). Sorption of NOR onto soil is influenced by soil organic matter and Cu(II) content (Zhang et al., 2009). Studies by Aristilde & Sposito indicate that, in soil, the metal cation involved in the fluoroquinolone–metal complex provides a cation bridge between the antimicrobial and the clay mineral, although the mechanism is not completely understood (Aristilde and Sposito, 2008). Therefore, sorption coefficients of fluoroquinolones (K_D, linear sorption distribution coefficient) are very high, reaching values up to 1000 L kg^{-1} in a study of Turkish agricultural soils (Uslu et al., 2008).

Most studies of antimicrobial sorption in soils have been carried out in northern temperate regions. The different environmental conditions found in the tropics, such as weather, predominance of low cation exchange capacity clays, lower soil organic matter and lower pH, may greatly affect the environmental behaviors of antimicrobials. The objective of this study was to investigate the sorption coefficients of NOR in four soils characteristic of the state of São Paulo, Brazil, using batch sorption kinetic experiments.

2. Materials and methods

2.1. Soil samples

Sorption studies of norfloxacin were carried out on four different soils characteristic of the state of São Paulo, Brazil: N1 (sandy), N2 (clay), S1 (sandy–clay) and S2 (clay).

Soils were collected in 2005 from different locations and transferred to lysimeters (1 × 1 × 2 m) located in the experimental area of the Brazilian Agricultural Research Corporation (Embrapa), Jaguariúna, SP, Brazil.

The origins of the soils were as follows:

N1 – sandy, city of Santa Rita de Passa Quatro, SP (21°42′18,12″S and 47°28′04,82″W, altitude 773 m) (pasture);
N2 – clay, city of Sertãozinho, SP (21°05′20,44″S and 47°48′10,73″W, altitude 538 m) (sugar cane plantation);
S1 –sandy–clay, city of Jaguariúna, SP (22°43′14,92″S and 47°01′14,20″W, altitude 617 m) (citrus plantation);
S2 – clay, city of Jaguariúna, SP (21°42′59,50″S and 47°01′00,05″W, altitude 609 m) (covered with *Brachiaria*).

The soils were collected from each lysimeter, air-dried, sieved to a particle size ⩽ 2 mm, and stored in plastic bags at room temperature until use. The physical and chemical characteristics of each soil are presented in Table 1.

2.2. Reagents and chemicals

Calcium chloride was supplied by Nuclear (Brazil). Norfloxacin (NOR; 1-Ethyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)-3-quinoline carboxylic acid; CAS Registry No. 70458-96-7; 99%) was purchased from Sigma–Aldrich, Belgium. The structural and physicochemical properties of NOR are shown in Table 2. Methanol (HPLC grade) was purchased from Tedia, USA. EDTA (Ethylenediamine tetraacetic acid, disodium salt) was purchased from J.T. Baker, USA. Acetic Acid was purchased from Nuclear, Brazil. Throughout the study, water was obtained from a Milli-Q purification system (Millipore, USA). A standard stock solution (1000 μg mL^{-1}) of NOR was prepared by dissolving 100 mg of NOR in 0.5 mL acetic acid and then diluted to 100 mL in a volumetric flask with 0.01 mol L^{-1} $CaCl_2$. Working solutions of NOR were

Table 1
Physical and chemical properties of the selected soils.

		Soil			
		N1	N2	S1	S2
pH (in 0.01 mol L^{-1} $CaCl_2$)		5.0	4.9	4.1	4.4
Depth of soil (cm)		0–20	0–20	0–20	0–20
Organic matter (%, w/w)		1.53	2.88	2.48	3.23
Organic carbon (%, w/w)		0.89	1.67	1.44	1.87
Iron (mg kg^{-1})		14	9	42	29
Cu (mg kg^{-1})		<0.1	5.4	0.8	0.8
Cation exchange capacity ($mmol_c$ kg^{-1})		19.3	52.7	51.9	66.0
Texture (%)	Sand (>0.053 mm)	91.1	14.9	52.9	43.5
	Silt (0.053–0.002 mm)	1.8	30.2	10.5	7.0
	Clay (<0.002 mm)	6.2	54.6	36.2	49.2