Science of the Total Environment 545–546 (2016) 48–56

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Adsorption and degradation of five selected antibiotics in agricultural soil

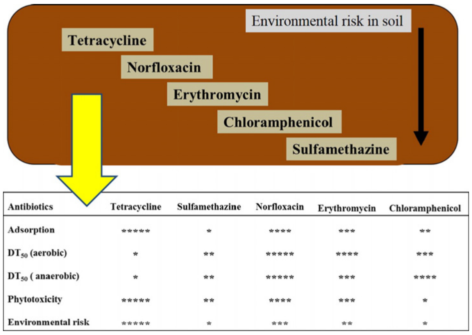
Min Pan, L.M. Chu *

School of Life Sciences, The Chinese University of Hong Kong, Shatin, NT, Hong Kong SAR, China

HIGHLIGHTS

- The persistence of antibiotics in soil was calculated
- Sterilized and non-sterilized soils under aerobic and anaerobic conditions were examined
- Higher concentration slowed down degradation and prolonged persistence in soil
- Degradation was related to their properties, microbial activities and soil aeration
- An equation was proposed to predict the fate of antibiotics in different soils

GRAPHICAL ABSTRACT



Antibiotics	Tetracycline	Sulfamethazine	Norfloxacin	Erythromycin	Chloramphenicol
Adsorption	*****	*	****	***	**
DT_{50} (aerobic)	*	**	*****	****	***
DT_{50} (anaerobic)	*	**	*****	***	****
Phytotoxicity	*****	**	****	***	*
Environmental risk	*****	*	***	**	*

ARTICLE INFO

Article history:
Received 7 October 2015
Received in revised form 8 December 2015
Accepted 8 December 2015
Available online 30 December 2015

Editor: Kevin V. Thomas

Keywords:
Antibiotics
adsorption affinity
microbial degradation
persistence
soil physicochemical properties
aerobic conditions
sterilized soil

ABSTRACT

Large quantities of antibiotics are being added to agricultural fields worldwide through the application of wastewater, manures and biosolids, resulting in antibiotic contamination and elevated environmental risks in terrestrial environments. Most studies on the environmental fate of antibiotics focus on aquatic environments or wastewater treatment plants. Little is known about the behavior of antibiotics at environmentally relevant concentrations in agricultural soil. In this study we evaluated the adsorption and degradation of five different antibiotics (tetracycline, sulfamethazine, norfloxacin, erythromycin, and chloramphenicol) in sterilized and non-sterilized agricultural soils under aerobic and anaerobic conditions. Adsorption was highest for tetracycline (K_d, 1093 L/kg), while that for sulfamethazine was negligible (K_d, 1.365 L/kg). All five antibiotics were susceptible to microbial degradation under aerobic conditions, with half-lives ranging from 2.9 to 43.3 d in non-sterilized soil and 40.8 to 86.6 d in sterilized soil. Degradation occurred at a higher rate under aerobic conditions but was relatively persistent under anaerobic conditions. For all the antibiotics, a higher initial concentration was found to slow down degradation and prolong persistence in soil. The degradation behavior of the antibiotics varied in relation to their physicochemical properties as well as the microbial activities and aeration of the recipient soil. The poor adsorption and relative persistence of sulfamethazine under both aerobic and anaerobic conditions suggest that it may pose a higher risk to groundwater quality. An equation was proposed to predict the fate of antibiotics in soil under different field conditions, and assess their risks to the environment.

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1. Introduction

For decades, antibiotics have been widely used worldwide to treat diseases and to protect the health of humans and animals (Sapkota et al., 2008). The consumption of antibiotics has been increasing in both industrialized and developing countries. In the US, veterinary antibiotics used in animal feeds increased from 90 t in 1950 to 9300 t in 1999 (AHI, 2002), and to 130,000 t for factory farms in 2009 (USFDA, 2012). In China, the production of total antibiotics was nearly 1,470,000 t in 2009 (Yang et al., 2010). Tetracyclines, sulfonamides, fluoroquinolones, macrolides and others are the most commonly used

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* Corresponding author.
E-mail address: leemanchu@cuhk.edu.hk (L.M. Chu).

http://dx.doi.org/10.1016/j.scitotenv.2015.12.040
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antibiotic types for both human and animals, and their usage was 12,000, 7920, 27,300, 42,200 and 38,400 t in 2013, respectively (Zhang et al., 2015). These antibiotics may be excreted as parent compounds and/or metabolites, and may enter the environment through the spreading of manures and biosolids on agricultural lands, direct deposition by grazing livestock, or discharge of wastewater, resulting in routine detection in soil, surface water, ground water, sediment and treated municipal wastewater (Chen et al., 2014; Yan et al., 2013). The presence of antibiotics in the environment can adversely affect the soil system. Tetracycline, sulfamethazine, norfloxacin, erythromycin, and chloramphenicol were studied as representatives of the commonly used antibiotic types, as they are widely used in human and animal medicines, and are frequently detected with relatively high concentrations in the environment (Sarmah et al., 2006; Yan et al., 2013). They are ionizable and can occur as neutral, zwitterionic, or charged (negative or positive) species under environmental conditions (Kahle and Stamm, 2007; Zhang and Dong, 2008; Zhao et al., 2011). These species have different chemical properties and mechanisms of adsorption and degradation in soil (Site, 2001). An understanding of their adsorption and degradation will provide vital insights into their persistence in soil and potential mobility from soil to the water column (through leaching or runoff). However, most of the studies have been carried out in aqueous environments and mainly focus on the degradation of antibiotics (Dorival-Garcia et al., 2013; Hektoen et al., 1995). Studies that examined both adsorption and degradation of antibiotics in agricultural soil are too few with most using unrealistically high concentrations (in mg/kg levels) to overcome limitations in measurement (Yang et al., 2009a, 2012; Zhao et al., 2011). Also, no model has been developed for speculating the adsorption and degradation of different types of antibiotics in agricultural soil and the environmental risks they may pose.

A comprehensive investigation of antibiotic adsorption and degradation is needed for a more complete understanding of the downward movement of antibiotics in soil. The objectives of this study were (1) to evaluate the adsorption and degradation of selected antibiotics in soil at environmentally relevant concentrations, (2) to study the relationship between their persistence in soil and their physicochemical properties, and (3) to derive an equation to predict their fate in soil under different field conditions. In the present study, the adsorption isotherm of selected antibiotics in the soil was determined. The mechanisms of degradation were investigated through comparative experiments using sterilized and non-sterilized soils under aerobic and anaerobic conditions with environmentally relevant concentrations in agricultural soil. Furthermore, based on the parameters obtained in the adsorption and degradation experiments, an equation would be derived to calculate the proportions of antibiotic adsorbed, degraded, and remained in the soil. The behaviors of other compounds in soil can also be evaluated to assess their environmental risks. This should be the first study to develop a model for the prediction of antibiotics in soil. Moreover, the estimated persistence in soil and environmental risks of the selected antibiotics were summarized. The results from the present study should help assess the environmental risks of antibiotics and other organic compounds in agricultural soil.

2. Materials and methods

2.1. Chemicals and soil

Tetracycline, sulfamethazine, norfloxacin, erythromycin, and chloramphenicol, which belong to five different types of antibiotics, were examined in this study (Table 1). All the standards used and some of the internal standards (sulfamethazine-d_4, norfloxacin-d_5, and erythromycin-$^{13}C_2$) were obtained from Sigma-Aldrich (USA); chloramphenicol-d_5 was purchased from Dr. Ehrenstorfer GmbH (Germany) and tetracycline-d_6 from Toronto Research Chemicals (Canada). Oasis HLB extraction cartridges (6 mL, 500 mg) (Waters Corporation, USA) were used to extract and purify target compounds. All organic solvents used were of HPLC grade and purchased from Merck Corporation (Germany). Individual stock solutions and internal standards were prepared at 100 mg/L in methanol and stored in amber glass vials at −20 °C.

The agricultural soil used in this study was collected from an organic farm (Produce Green, Hong Kong) at the 0–20 cm depth, which was sieved through a 2 mm sieve after air drying. It was a clay loam with a pH of 6.45, 0.80% organic carbon content (f_{oc}) and 50% maximum water holding capacity. The bulk density (ρ_b) was 1.39 g/cm^3 and porosity (θ) 0.45. Soil texture, bulk density and porosity were determined according to the methods by American Society for Testing and Materials (ASTM, 2006, 2007; ATSM, 2009). Soil pH value was measured by a pH meter in distilled water (1:1). Organic carbon was analyzed using a TOC analyzer (Shimadzu, Japan). The maximum water holding capacity was determined according to the guideline of International Organization for Standardization (ISO, 2012). To determine the role of soil microorganisms in antibiotic degradation, a subsample was sterilized by autoclaving at 121 °C for 45 min over three consecutive days.

2.2. Adsorption experiment

Batch adsorption experiments were performed according to the guideline of the Organization for Economic Co-operation and Development (OECD, 2000). A total of 25 mL $CaCl_2$ solution (0.01 M) containing the five selected antibiotics and 5 g agricultural soil (dry weight) was added to 50 mL centrifuge tubes. The soil samples were spiked with 20 μL antibiotic solutions to yield initial nominal concentrations of 10, 20, 40, 60, 80, and 100 μg/L for each antibiotic in the aqueous phase. To inhibit microbial activity, sodium azide (25 μg) was added into each sample. The initial pH of the solution was adjusted by HCl and NaOH solutions to 6.45 ± 0.50. All the centrifuge tubes were shaken in an orbital shaker (Lab-line 3527–1 Environ shaker) at 180 rpm and 25 ± 1 °C for 24 h to obtain equilibrium. All procedures were conducted in the dark to avoid photodegradation. After equilibrium was achieved, the tubes were centrifuged at 8820 × g for 10 min. The supernatant was then filtered through a 0.2 μm syringe filter before HPLC-MS/MS analysis. All experiments were conducted in triplicates. Blank samples containing an equivalent amount of soil and a total aqueous solution volume of 25 mL (without antibiotics), and soil-less, antibiotic-only controls were subjected to the same experimental procedures. These were used as background controls to detect any interfering compound or contamination originating from the soil or the aqueous solution.

The concentration of an antibiotic (C_w, μg/L) in the supernatant was determined after equilibrium was achieved and C_s (μg/kg) is the equilibrium concentration of antibiotic adsorbed in soil. The adsorption coefficient K_d (L/kg) was calculated using the following equation (Xu et al., 2009):

$$K_d = C_s/C_w$$

The organic carbon adsorption coefficient K_{oc} value for each antibiotic was calculated by the equation: $K_{oc} = K_d/f_{oc}$. Freundlich isotherm was used to test the linearity of adsorption coefficient over a range of concentrations (Xu et al., 2009):

$$C_s = K_f * C_w{}^n$$

where K_f is the Freundlich adsorption coefficient of a given substance and n is the Freundlich exponent which indicates whether the

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