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Leaching behavior of veterinary antibiotics in animal manure-applied soils

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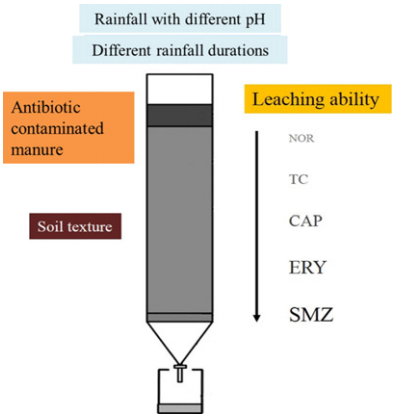
HIGHLIGHTS

- The leachability of VAs in soil was assessed.
- Rainfall situation, VA concentration (500–8000 μg/kg) and soil texture were examined.
- Rainfall pH and duration affected migration of VAs in soil.
- Two models (Cohen and Gustafson) were tested to predict the leaching of VAs in soils.

GRAPHICAL ABSTRACT



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ABSTRACT

Agricultural fields worldwide are being contaminated by the escalating application of veterinary antibiotics (VAs) via animal manure and biosolids applied as fertilizers or of wastewater for irrigation, resulting in soil degradation and damage to the health of terrestrial environments. This paper describes a series of column studies investigating the leaching behavior of five VAs, tetracycline (TC), sulfamethazine (SMZ), norfloxacin (NOR), erythromycin (ERY) and chloramphenicol (CAP), under different simulated rainfall conditions that could occur in agricultural environments. Our aim was to explore the effects of acid rain and torrential rain on the leaching of different VAs and to determine their leaching behaviors along the soil profile. The results showed that acid rain accelerated the accumulation of VAs from animal manure in surface soil while long rainfall durations promoted the downward migration of VAs in soil. Under acid rain conditions, a higher concentration of VAs remained in the animal manure. More VAs were eluted to deeper soil layers and the leachate under extreme rainfall conditions. The leachability of VAs was higher in sandy soil than in clay or loamy soil. SMZ and ERY posed a higher risk to deeper soil layers and groundwater, while NOR and TC tended to persist in surface soil, which can be explained by their different physicochemical properties in soil. Moreover, the general trends from two model assessments and soil column measurements appeared to be in agreement. SMZ had a high leachability, while NOR tended to accumulate in soils. This study provided vital insight into the persistence mechanisms of VAs in terrestrial environments and their potential risks to soils and groundwater.

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1. Introduction

Veterinary antibiotics (VAs) have been widely used to treat diseases and to protect the health of animals for several decades (Sapkota et al., 2008). The global consumption of VAs by livestock in 2010 was at least 63,000 tons and was projected to rise to 106,600 tons in 2030 (Van Boeckel et al., 2015). As most VAs undergo metabolic changes in animals, approximately 90% of them are excreted in urine and 75% in animal feces in one dose (Halling-Sørensen, 2001). Thus, VAs may be excreted as the parent compounds and/or metabolites, which enter into the environment through the spreading of animal manure on agricultural land, direct deposition by grazing livestock, and the discharge of wastewater. It is evident that VAs have harmful effects on terrestrial and aquatic environments via the application of animal manure as fertilizer on agricultural land, which is followed by surface runoff and leaching into deeper soil layers (Ji et al., 2012; Li et al., 2015). More than 30 VAs have been found in soil, surface water, ground water, sediment and even drinking water (Chen et al., 2014; Yan et al., 2013). The concentrations of VAs can be as high as 307 μg/kg in soil and 15 μg/L in ground and surface water, respectively (Hamscher et al., 2002; Lindsey et al., 2001). Tetracyclines, sulfonamides, fluoroquinolones, macrolides and others are the most common types of antibiotics used in China in both humans and animals, and their usage was 12,000, 7920, 27,300, 42,200, and 38,400 tons in 2013, respectively, (Zhang et al., 2015). Tetracyclines, sulfonamides and macrolides are the most common VAs present in swine, cattle and poultry manure in China, the concentrations of which range from 0.01 to 1420 mg/kg (Chen et al., 2012; Zhao et al., 2010).

The leaching and adsorption behaviors of VAs in agricultural soils could be affected by acid rain and subsequent soil acidification, which have been major environmental issues in China in recent years, as pH affects the fraction of ionized VAs in the soil (Figueroa-Diva et al., 2010; Srinivasan et al., 2013b). Rainfall pH ranges from 4.72 to 6.33, and >70% of the cities in Guangdong Province suffered from acid rain in 2014 (DEPGP, 2015). In addition, global warming may cause extreme weather events such as droughts, floods, heat waves and heavy rain to occur more frequently (CMA, 2015; GMS, 2015). The intensity and duration of torrential rain and the maximum daily precipitation have also increased in recent years (CMA, 2015). The expanding range of acid rain, its decreasing pH, and more frequent extreme rainfall events may affect the migration of VAs from animal manure to deeper soil layers and/or groundwater (GMS, 2015). However, previous studies were not able to determine the leaching mechanisms of VAs by examining their physicochemical properties (e.g., adsorption and degradation) and soil properties (Brown et al., 2000; Ostermann et al., 2013). Additionally, very few studies have examined the vertical migration of veterinary medicines from animal manure to soils under varying rainfall situations (acid rain and extreme weather). It is therefore necessary to assess the leachability of VAs in soils of different texture under varying rainfall situations and to determine their potential risks of being leached to groundwater or transferred to edible crops, which are consumed by humans.

The objectives of this study were (1) to assess the effect of animal manure fertilization on antibiotic leaching in soil; (2) to explore the effects of acid rain and torrential rain on the leaching of different VAs in soil; (3) to study the effect of soil texture on the downward movement of VAs by modeling; and (4) to determine the potential risks associated with different VAs in soil using two screening models. We adopted a series of column studies to elucidate the mechanisms of VA leaching using different rainfall factors, VA concentrations in animal manure and soil types. Understanding the potential transport of different VAs in soils under varying rainfall situations is necessary to provide insight into their persistence and migrations in terrestrial environments as well as to evaluate their potential risks to soils and groundwater.

2. Materials and methods

2.1. VAs and chemicals used

The leachability of tetracycline (TC), sulfamethazine (SMZ), norfloxacin (NOR), erythromycin (ERY) and chloramphenicol (CAP), which belong to five different types of VAs, was examined (Table 1). All standards and some internal standards (sulfamethazine-d_4, norfloxacin-d_5 and erythromycin-$^{13}C_2$) were obtained from Sigma-Aldrich (USA). Chloramphenicol-d_5 was obtained from Dr. Ehrenstorfer GmbH (Germany), while tetracycline-d_6 was purchased from Toronto Research Chemicals (Canada). Oasis HLB extraction cartridges (6 mL, 500 mg) (Waters Corporation, USA) were used for the extraction and purification of the target VAs. All the organic solvents used were of HPLC grade 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.

2.2. Soils and animal manure used

Sandy soil was collected from a construction site in Ho Man Tin (Kowloon), loamy soil was collected from an organic farm in Hok Tau (New Territories), and clay soil was collected from an arable farm in Long Valley (New Territories). None of the soils had any history of application of manure that contained VAs, and no target compounds were detected in the soil samples. The physicochemical properties of the three soils are listed in Table 2, which were determined according to the methods described by the American Society for Testing and Materials (ASTM, 2007; ATSM, 2009).

Chicken manure was collected from an organic animal farm in Huizhou (Guangdong, China) that is accredited by the Guangdong Provincial Department of Agriculture as animal-drug free. No target compounds were detected in the chicken manure samples. A certain amount of VAs was added to each portion of chicken manure slurry.

2.3. Experimental setup of the soil column leaching tests

All tests were done according to the OECD's guidelines for leaching in soil columns (OECD, 2004). Soil column leaching tests are a common laboratory-scale method for investigating the fate of VAs in the environment (Kay et al., 2005a; Sadeghi et al., 2000). PVC columns 60 cm in length and with an internal diameter of 10 cm (Fig. 1), each containing 1500 g of air dried and sieved soils (<2 mm) supported on nylon mesh at the bottom of each column, were used. Each column sat on an HDPE funnel which drained into a 500-mL amber glass bottle for collecting the leachate, which was stored at −18 °C before analysis. To obtain uniform packing, the soil was added in small amounts under gentle vibration of the column to give a highly homogeneous reconstructed soil mass. Each treatment was replicated three times. The soil columns were acclimatized for one month and maintained at >60% of their maximum field capacity with artificial rain (0.01 mol/L $CaCl_2$) (Kay et al., 2005a). The chicken manure slurry was added to the soil surface. During the experiment, the soil columns were covered with a black cloth to avoid photodegradation, and kept at a temperature of 25 ± 2 °C in a ventilated greenhouse. The soils were sampled at depths of 0 to 50 cm at the end of the experiment from sealed perforations made on the soil column at the corresponding depths. They were then sectioned into five depths, namely 0–10, 10–20, 20–30, 30–40 and 40–50 cm.

2.4. Rainfall conditions

Four treatments were used to investigate the leaching of VAs in soils under different rainfall conditions. A total amount of 393 mL of artificial rain, corresponding to 50 mm heavy rain, was added drop wise within 24 h to each column. A glass sinter disk was placed on top of the column to ensure even distribution of the artificial rain. The amount of chicken