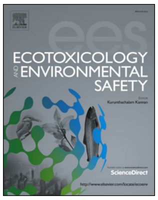
Ecotoxicology and Environmental Safety 165 (2018) 376–385

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

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



Systematic analysis of occurrence and variation tendency about 58 typical veterinary antibiotics during animal wastewater disposal processes in Tianjin, China

Suli Zhi[a], Jing Zhou[b], Fengxia Yang[a], Liang Tian[c], Keqiang Zhang[a,*]

[a] *Agro-Environmental Protection Institute, Ministry of Agriculture, Tianjin 300191, China*
[b] *College of Resources and Environment, Northeast Agricultural University, Harbin 150036, China*
[c] *School of Energy and Environmental Engineering, Hebei University of Technology, Tianjin 300132, China*

ARTICLE INFO

Keywords:
Veterinary antibiotics
Variation tendency
Relationship
Mass loading
Animal farm

ABSTRACT

Residue of veterinary antibiotics (VAs) in the animal breeding industry has become a problematic environmental issue. However, the residual levels of VAs as well as their variation tendency, degradation mechanisms and relationships with other parameters during animal wastewater disposal processes are still obscure. This study measured different samples during wastewater disposal processes from three farms, and systematically analyzed the residue, migration and removal of 58 kinds of typical VAs (6 classes) in Tianjin, China. The results showed that about 44 kinds of VAs were quantitatively detected. Tetracycline antibiotics (TCs) usually had higher residual concentrations than other classes of VAs in the raw wastewater; the highest residual concentration was 130.67 ± 5.90 μg/L which occurred for chlortetracycline (CTC). Pig farms generally had more VAs species and higher residual concentrations than dairy farms, and the proportion of different VAs was similar for dairy farms. The final removal rates of different VAs classes varied largely (negative to > 99.87%), and the highest removal rates usually occurred in biological processes for adsorption and biodegradation effects, and occasionally occurred in the final effluents. The correlation coefficients between VAs removal rates and chemical oxygen demand (COD) removal rates were much higher than those of total nitrogen (TN), total phosphorus (TP) and ammonia nitrogen (NH_4-N) in pig farms, while opposite conclusion was obtained in dairy farms. Among different classes, TCs presented the highest daily mass loading of ND ~ 10,453.8 ± 471.7 mg/d in the influent and ND ~ 1141.6 ± 58.9 mg/d in the effluent in farm 1.

1. Introduction

Antibiotics have been widely used in the animal breeding industry worldwide, for preventing purpose, treating diseases, and promoting growth of livestock animals as feed additives (Huang et al., 2017; Zhou et al., 2013a; Wei et al., 2011). China is one of the largest animal producers worldwide (Wei et al., 2011), with more than 463 million pigs and 106 million cattle in the country (Zhou et al., 2013b), which account for 51.6% and 8% of the total numbers in the world respectively (NBS (National Bureau of Statistics of China), 2012). Besides, market sales data show that China is the largest producer and consumer of antibiotics in the world (Zhu et al., 2013), and it was estimated that about 162,000 t of antibiotics were used in China in 2013 (Zhang et al., 2015), among which 52% were used for livestock animal breeding. More importantly, many studies have demonstrated that 30-90% of these antibiotics were excreted with feces and urine for partially metabolized by animal body, in form of parent compounds, conjugates, oxidation or hydrolysis products (Wei et al., 2011; Liu et al., 2013; Chen et al., 2017). Therefore, animal waste, especially wastewater, may contain high amounts of these veterinary antibiotics (VAs) compounds.

In animal farms of China, a large volume of wastewater is usually produced, from urine and flushing water. Urine generally contains residual antibiotics that are mainly discharged from animal bodies. Flushing water usually contains high amounts of antibiotic residues, because it contacts animal manure which results in antibiotic residues into liquid part from animal feces after solid-liquid separation. Thus, animal wastewater is a kind of hard disposal waste, not only for its large volume production but also for it's a major source of antibiotic residues. Up to now, studies on the antibiotic residues in wastewater have focused mainly on three aspects. (1) The first aspect involves monitoring antibiotic residues in animal wastewater. Some studies have involved antibiotic residues detection in animal wastewater. For example, Chen

---

* Corresponding author.
E-mail addresses: zhisuli87@163.com (S. Zhi), keqiangzhang68@163.com (K. Zhang).

https://doi.org/10.1016/j.ecoenv.2018.08.101
Received 18 December 2017; Received in revised form 23 August 2018; Accepted 28 August 2018

et al. (2012) showed that residual antibiotic concentrations could reach 685.0 μg/L in swine wastewater; while Zhou et al. (2013b) reported that the residual concentrations of seventeen antibiotics in swine wastewater were in the range of 13.7 ± 1.95 ng/L to 166 ± 27.4 μg/L. However, these studies did not show the variation tendency of VAs during wastewater disposal processes, and could not provide insight into the removal efficiencies and effluent concentrations of VAs which may become a new pollution source for other environmental mediums. (2) The second aspect involves the removal of antibiotic residues in animal wastewater. Several studies have focused on the ability of constructed wetlands to reduce/remove various antibiotics present in animal wastewater. Almeida et al. (2017a, 2017b) showed that the removal rate of VAs could be up to 90% by constructed wetland. Huang et al. (2017) studied the effects of VAs on the performance and bacterial community of vertical flow constructed wetlands. But these studies mainly focused on the VAs removal during a specific process, such as constructed wetland. (3) The third aspect involves the variation tendency of antibiotics during disposal processes. Actually, many experiments involving this phenomenon do exist, but they just focused on municipal wastewater treatment plants (Jia et al., 2012; Junker et al., 2006; Zhou et al., 2013c). From the above three aspects, we can see that studies on the variation tendency of VAs in animal wastewater undergoing the disposal processes are really scarce.

With development of the production scale and the intensity of animal husbandry industry, the pollution caused by animal farms has been paid more and more attention. In China, the treatment mode of “combining planting and breeding” is currently advocated, and wastewater is treated by a series of processing techniques before farmland use. However, few studies investigate the variation of veterinary antibiotics during these processing techniques. Moreover, the VAs species studied in existing reports was relatively limited (Almeida et al., 2017a, 2017b; Huang et al., 2017). Liu et al. (2013) investigated the elimination of three kinds of VAs (ciprofloxacin, oxytetracycline and sulfamethazine) from swine wastewater in vertical flow constructed wetlands. Using an intermittently aerated sequencing batch reactor, Zheng et al. (2018) studied the removal of 11 VAs from swine wastewater. The present study investigated the variation tendency of 58 VAs during a series of processes.

To comprehensively understand the transformation rules of VAs, this study selected three representative farms in Tianjin, China, which have a set of combinatorial processes to ensure effluent safety for land use. The variation of 58 antibiotics in these farms was studied under normal operating conditions. The aims of the study are to elucidate the VAs pollution situation in farms, the transformation rules between different VAs classes and different farms, the degradation mechanisms of different VAs species, and to understand the relationships between the removal of antibiotics and the removal of other parameters.

2. Materials and methods

2.1. Materials

All antibiotics used, including 58 kinds of VAs belonging to 6 classes, were analytical standard. There were 5 kinds of tetracyclines antibiotics (TCs), 19 kinds of sulfonamides antibiotics (SAs), 13 kinds of quinolones antibiotics (QAs), 6 kinds of aminoglycosides antibiotics (AAs), 9 kinds of β-lactams antibiotics (LAs) and 6 kinds of macrolides antibiotics (MAs). TCs contained chlortetracycline (CTC), tetracycline (TC), oxytetracycline (OTC), doxycycline (DOX) and demeclocycline (DEM). SAs involved in sulfamoxole (SAM), sulfamethoxazole (SMX), sulfamethizole (SMZ), sulfathiazole (STZ), sulfisoxazole (SIX), sulfadiazine (SDZ), sulfadimidine (SDM), sulfamerazine (SMA), sulfadimethoxine (SDT), sulfisomidine (SIM), sulfameter (SM), sulfamonomethoxine (SMM), sulfapyridine (SPD), sulfabenzamide (SBZ), sulfacetamide (SCM), sulfadoxine (SDX), sulfaguanidine (SGN), sulfamethoxypyridazine (SMP) and sulfaquinoxaline (SQX). QAs included enrofloxacin (ENR), ciprofloxacin (CIP), norfloxacin (NOR), danofloxacin (DAN), ofloxacin (OFL), enoxacin (ENO), sarafloxacin (SAR), difloxacin (DIF), flumequine (FLU), lomefloxacin (LOM), nalidixic acid (NAL), orbifloxacin (ORB) and oxolinic acid (OXO). AAs contained amikacin (AMI), apramycin (APR), neomycin (NEO), spectinomycin (SPE), streptomycin (STR) and tobramycin (TOB). LAs contained amoxicillin (AMOX), ampicillin (AMP), cloxacillin (CLX), dicloxacillin (DCLX), dihydrostreptomycin (DHDS), nafcillin (NAF), lincomycin (LIN), penicillin G (PENG) and penicillin V (PENV). MAs contained azithromycin (ATM), clarithromycin (CTM), erythromycin (ETM), roxithromycin (RTM), spiramycin (SPM) and tilmicosin (TMC). All VAs were purchased from Dr. Ehrenstorfer Gmbh (Augsburg, Germany). The purity of the standards was all greater than 98%. Acetonitrile (ACN), methanol (MeOH) and formic acid (HPLC grade) were purchased from ROE Scientific, Inc. (Newark, USA). Disodium ethylenediaminetetraacetate (Na_2-EDTA) was purchased from Xilong Chemical Co., Ltd. (Guangdong, China). N-EVAP 112 nitrogen evaporator with water bath and gas nozzles was obtained from Oganomation Associates Inc., USA. Rotary evaporator was obtained from a factory in Shanghai, China. Individual stock solutions of all standards were prepared by dissolving certain quality of each antibiotic in a certain volume of MeOH. The stock solutions were stored in amber glass bottles at − 20 °C. Working standard mixtures were prepared by diluting each stock solution together.

2.2. Introduction of sampling farms

2.2.1. Breeding situation of sampled farms

Tianjin is a typical big city in northeast China, with an area of 11,860.63 km^2. It is a major base of animal and vegetable production for the surrounding regions. In 2015, the numbers of slaughtered pigs and cattle were 378.00×10^4 and 19.62×10^4 respectively. In addition, the mode of livestock and poultry breeding is becoming more and more intensive. Three representative farms in Tianjin of China were selected to analyze the VAs pollution, migration and variation trends of VAs. The locations of these three farms are shown in Fig. S1. The specific wastewater treatment processes for these three farms are shown in Fig. S2. Each farm has five sampling sites, which are also marked in Fig. S2.

2.2.1.1. Farm 1: pig farm. Farm 1 is a pig farm and was founded in 2006, with an area of 56.7 ha. At present, the integrated industrial chain of planting, breeding, slaughtering, processing and marketing has been implemented in this farm. It has a disposable storage of about 12,000 pigs. The annual sales of boar and commercial pigs are about 20,000 pigs.

2.2.1.2. Farm 2: dairy cattle farm. Farm 2 is a typical large-scale dairy cattle farm, with an area of 5.3 ha. The farm is divided into production section, office living section, feed storage and waste disposal section. It currently has 850 Holstein dairy castles, including 500 adult cows and 350 replacement cows.

2.2.1.3. Farm 3: dairy cattle farm. Farm 3 is a typical large-scale dairy cattle farm, with an area of 12.0 ha. The farm has 2 cattle houses, 1 milking room and 1 warehouse. Now it has 850 dairy castles, including 400 lactating cows, 340 replacement cows and 110 other cows.

2.3. Sample collection, preparation and analysis

2.3.1. Sample collection

Wastewater samples were collected from the sampling sites as shown in Fig. S2. The samples were collected in 500 ml amber glass bottles from three farms during three consecutive days on September 25–27, 2016 (no rain). A composite sampling method was adopted during the sampling days, to avoid the error caused by discontinuous of