Science of the Total Environment 612 (2018) 358–367

Contents lists available at ScienceDirect

Science of the Total Environment

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

Monitoring tylosin and sulfamethazine in a tile-drained agricultural watershed using polar organic chemical integrative sampler (POCIS)

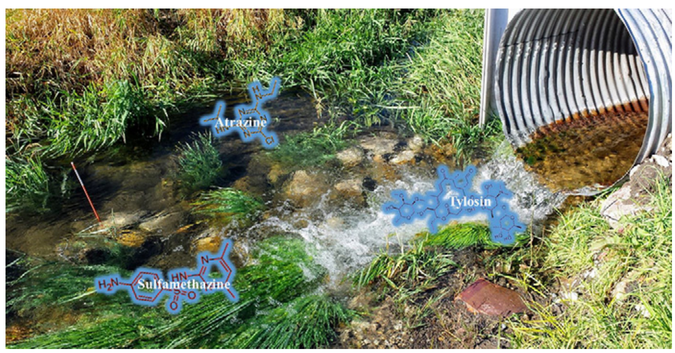
Maurice T. Washington [a], Thomas B. Moorman [b,*], Michelle L. Soupir [a], Mack Shelley [c], Amy J. Morrow [b]

[a] Department of Agricultural and Biosystems Engineering, Iowa State University, 1340 Elings Hall, 605 Bissell Road Ames, Iowa, USA
[b] National Laboratory for Agriculture and the Environment, USDA-ARS, 2110 University Boulevard Ames Iowa, 50011, USA
[c] Department of Political Science and Department of Statistics, 503 Ross Hall, Iowa State University, Ames, Iowa, USA

HIGHLIGHTS

- Tylosin and sulfamethazine were detected in 37 to 100% of samples at four locations.
- Time weighted antibiotic concentrations were less than 2 ng L^{-1} and were markedly less than the atrazine concentration.
- Direct sampling of the subsurface drainage water showed that antibiotics are leaching through the soil profile.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 May 2017
Received in revised form 8 August 2017
Accepted 9 August 2017
Available online 1 September 2017

Editor: Jay Gan

Keywords:
Tile-drainage
POCIS
Antibiotics
Tylosin
Sulfamethazine
Atrazine

ABSTRACT

This study evaluated the influence of temporal variation on the occurrence, fate, and transport of tylosin (TYL) and sulfamethazine (SMZ); antibiotics commonly used in swine production. Atrazine (ATZ) was used as a reference analyte to indicate the agricultural origin of the antibiotics. We also assessed the impact of season and hydrology on antibiotic concentrations. A reconnaissance study of the South Fork watershed of the Iowa River (SFIR), was conducted from 2013 to 2015. Tile drain effluent and surface water were monitored using polar organic integrative sampler (POCIS) technology. Approximately 169 animal feeding operations (AFOs) exist in SFIR, with 153 of them being swine facilities. All analytes were detected, and detection frequencies ranged from 69 to 100% showing the persistence in the watershed. Antibiotics were detected at a higher frequency using POCIS compared to grab samples. We observed statistically significant seasonal trends for SMZ and ATZ concentrations during growing and harvest seasons. Time weighted average (TWA) concentrations quantified from the POCIS were 1.87 ng L^{-1} (SMZ), 0.30 ng L^{-1} (TYL), and 754.2 ng L^{-1} (ATZ) in the watershed. SMZ and TYL concentrations were lower than the minimum inhibitory concentrations (MIC) for *E. coli*. All analytes were detected in tile drain effluent, confirming tile drainage as a pathway for antibiotic transport. Our results identify the episodic occurrence of antibiotics, and highlights the importance identifying seasonal fate and occurrence of these analytes.

1. Introduction

Antibiotics have been used in livestock production since the early 1950's for growth promotion (subtherapeutic), disease prevention

* Corresponding author.
E-mail address: tom.moorman@ars.usda.gov (T.B. Moorman).

http://dx.doi.org/10.1016/j.scitotenv.2017.08.090

(prophylactic), and disease treatment (therapeutic use). In 2013, the total dispersal of approved antibiotics for food producing livestock was approximately 14.9 million kilograms, in which 99.3% of that total dispersal was used, domestically in the United States (FDA, 2015). In a five-year span between 2009 and 2013, the domestic sale and distribution of antibiotic active ingredients for agricultural use increased approximately 17%, while those classified as medically important increased 20% (FDA, 2015).

Subtherapeutic use of antibiotics in animal feed and water for growth promotion is a concern due to their ability to select resistant bacteria in the gastrointestinal tract of livestock (Chee-Sanford et al., 2009). These antibiotics are not fully metabolized in livestock and are excreted as the parent compound or as a metabolite (Kim et al., 2011; Joy et al., 2013; Kemper, 2008). Antibiotics enter the environment via land application of manure or lagoon treated water (Kim and Carlson, 2007). Once delivered into the terrestrial environment, their potential to induce antibiotic resistance is a cause for concern. Recently, the U.S Federal Drug Administration (FDA) introduced a strategy to combat antibiotic resistance, with the issuance of "Guidance for Industry" (GFI) documents #209 (FDA, 2012) and #213 (FDA, 2013) and the Veterinary Feed Directive (VFD). The VFD requires the supervision of a licensed veterinarian for the use of drugs in or on animal feed. Currently, all antibiotics ranked under GFI #152 (FDA, 2003) are classified as medically important to human health, and include the macrolide antibiotic tylosin and the sulfonamide antibiotic sulfamethazine.

To investigate the potential relationship between antibiotic resistance and low environmental concentrations, monitoring strategies are needed to detect these low concentrations. Pruden et al. (2013) suggests that strategic monitoring is needed to provide baseline data on antibiotics, residues, and antibiotic resistance genes (ARGs). Since the first national reconnaissance pharmaceutical water quality study (Kolpin et al., 2002) the investigation of the occurrence, fate, and transport of emerging contaminants has become more prevalent. From this study and others, antibiotics have been detected in surface water (Fairbairn et al., 2015; Ou et al., 2015; Gao et al., 2012), ground water (Barber et al., 2008; Campagnolo et al., 2002; Watanabe et al., 2010), soil (Joy et al., 2013; Kurwadkar et al., 2011), sediment (Gao et al., 2012; Ok et al., 2011; Kim and Carlson, 2007), and crops (Carter et al., 2014; Bassil et al., 2013; Wu et al., 2011; Jones-Lepp et al., 2012; Dolliver et al., 2007).

Water quality monitoring of antibiotics and other emerging contaminants is difficult due to their diverse physiochemical properties and their interactions in the environment. Traditional environmental sampling techniques including discrete grab samples and automatic samplers have been used for emerging contaminants. These sampling techniques often require extracting large volumes of water to detect these contaminants (Söderström et al., 2009 and Alvarez et al., 2005). The greatest shortcoming of discrete grab sampling, is that it only provides a snapshot of environmental levels, neglecting episodic events and overestimating concentrations. The use of these sampling methods can be expensive and time-consuming (Söderström et al., 2009; Alvarez et al., 2007). The development of passive sampler technology such as the Polar Organic Chemical Integrative Samplers (POCIS) has potentially provided a better alternative for sampling polar organic contaminants such as tylosin, sulfamethazine, and atrazine.

The POCIS is a dynamic monitoring tool, which has the ability to detect ultra-low concentrations of the dissolved phase of chemicals. The POCIS has three general designated uses: screening of pollutants, determination of TWA concentrations, and toxicity bioassay analysis. The screening capability of the POCIS allows for the determination of the source and concentration gradient of chemicals. The application of screening and TWA determination allows for the evaluation of spatial and temporal distribution in aquatic environments (Morin et al., 2012; Söderström et al., 2009). The ability of the POCIS to screen pollutants was also shown in a study conducted by Kolpin et al. (2013) where POCIS were used to determine the exposure of chemical contaminants to smallmouth bass in the Potomac River basin. Among the chemical contaminants tylosin, sulfamethazine, and atrazine detection frequencies were 0, 40, and 100% respectively. Recently, Jaimes-Correa et al. (2015) used the POCIS to determine the seasonal occurrence of 12 different antibiotics, including tylosin and sulfamethazine, and a beta agonist in a predominantly agricultural watershed in Nebraska. The tylosin and sulfamethazine did not show any spatial or temporal variation in that watershed. Morin et al. (2012) has noted the application of the POCIS to the detection and quantification of an estimated 300 chemicals. The POCIS is an extensive tool that has been used in many aquatic environments including: rivers, streams, creeks, estuaries, lakes, seas, bays, and harbors.

We conducted a reconnaissance study of the SFIR, to establish the baseline water quality levels in respect to sulfamethazine (SMZ) and tylosin (TYL), and determine their distribution in the watershed using POCIS technology. Our objectives were to investigate the influence of temporal and spatial variation on the occurrence, fate, and transport of tylosin and sulfamethazine; determine the frequency of detection, and assess the impact of tile drainage vs. surface water on antibiotic loads and concentrations. Tylosin and sulfamethazine were chosen because they are used in swine production and we had previously detected tylosin in agricultural drainage water (Garder et al., 2014). Atrazine was included as a reference compound as it has often been detected in agricultural watersheds.

2. Materials & methods

2.1. Watershed description

The South Fork watershed (SFIR) is a predominantly agricultural watershed, which encompasses approximately 78,000 ha (193,000 acres). The greater part of SFIR is located in Hamilton and Hardin counties in north central Iowa, with the most northern part located in Wright and Franklin counties. Three major drainage areas make up the SFIR; Tipton Creek tributary in the southwest, South Fork of the Iowa River in the center, and the Beaver Creek tributary in the southeast. The headwaters of the South Fork of the Iowa River originate from three subsurface drains located in Hamilton County. From the headwaters, the South Fork flows in a northeasterly direction until entering Hardin County where it flows in a southeasterly direction meeting the Iowa river south of Eldora (McCarthy et al., 2012).

The SFIR is dominated by agricultural land covering approximately 96% of the watershed. There is a large concentration of animal production facilities along with intense row cropping. There are approximately 169 animal feeding operations (AFOs) in the watershed, with 153 of them being swine facilities (Fig. 1), accounting for 91% of AFOs. Swine seem to have a higher frequency of bacteria with antibiotic resistant genes (ARG), which directly correlates with the amount of antibiotics used by the swine industry compared to cattle or sheep (Heuer et al., 2011). Swine manure produced from treated pigs, has been shown to enhance the spread of antibiotic resistance in soil bacterial communities (Heuer et al., 2011). Campagnolo et al. (2002) showed that antibiotics are transported from swine farms to proximal surface and ground water. The prevalence of antibiotic resistant bacteria was further documented in swine herds by (Chander et al., 2007; Mathew et al., 2001). According to Tomer et al. (2008a), the estimated swine population of the watershed is 601,193 (Beaver Creek: 75,379, South Fork: 301,628, and Tipton Creek: 224,186). The resulting swine densities are 4.14 (Beaver Creek), 7.9 (South Fork), and 11.29 (Tipton Creek) swine ha^{-1}. More recently Hamilton and Hardin counties were estimated to have a swine inventory of 1.37 million (USDA-NASS, 2012). Previous work shows that the SFIR contains persistent populations of *E coli* and *Enterococcus* (Tomer et al., 2008a), and genes associated with zoonotic pathogens (Givens et al., 2016), suggesting that transport of antibiotics within this watershed is likely. Finally, three small towns with a combined human population of <500 have sewage treatment facilities the