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Research Paper

Transport mechanisms for veterinary pharmaceuticals from beef cattle feedyards to wetlands: Is aerial deposition a contributing source?☆

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A B S T R A C T

Veterinary pharmaceuticals from beef cattle feedyards have, with increasing frequency, been identified as contaminants in aquatic systems. Transport of these pharmaceuticals has generally been assumed to be via manure land application, surface runoff, or groundwater percolation. However, veterinary pharmaceuticals in airborne particulate matter downwind of beef cattle feedyards have recently been documented, indicating that aerial transport and deposition are a potential transport mechanism in arid and semi-arid environments. In this study, 35 hydrologically discrete playa wetlands within 15 km of beef cattle feedyards were examined for occurrence of six steroid hormones and eight antibiotics. 17α-trenbolone, estrone, estradiol, tetracycline, chlortetracycline, oxytetracycline, tylosin, and monensin were all detected in either water or sediment samples. Concentrations for the majority of analytes were < 15 ng/g in sediment and < 70 ng/L in water. Tylosin and monensin were detected at highest concentrations in water, at 3 and 84 μg/L, respectively. A correlation between distance from the nearest beef cattle feedyard and concentration of monensin in playa water was observed, similar to correlations observed between pharmaceutical concentrations and distance from feedyard among air samples collected downwind of feedyards. This study suggests that airborne transport and deposition of pharmaceutical-laden particulate matter are a possible contributor to pharmaceutical concentrations in aquatic systems. Aerial deposition of pharmaceutical-laden particulate matter, not typically included in risk assessments, is of yet poorly characterized but may play a significant role in pharmaceutical transport in arid and semi-arid locations and deserves further investigation.

1. Introduction

Use of pharmaceuticals for veterinary purposes, such as prophylaxis and growth promotion, constitutes a large proportion of total global pharmaceuticals. Numerous studies have documented the occurrence of veterinary pharmaceuticals in aquatic systems impacted by animal agriculture (Durhan et al., 2006; Kim and Carlson, 2006; Lissemore et al., 2006; Kolok et al., 2007; Bartelt-Hunt et al., 2011; , 2012; Zhang et al., 2013; Bak and Björklund, 2014; Cavallin et al., 2014; Chen and Zhou, 2014; Cheng et al., 2014; Gall et al., 2014; Xu et al., 2014; Jaimes-Correa et al., 2015; Hafner et al., 2016). Transport of biologically active chemicals therefore raises concern for adverse effects among aquatic species (Soto et al., 2004; Jensen et al., 2006; Kidd et al., 2007; Sellin et al., 2009; Jeffries et al., 2011; Baumann et al., 2014; Sangster et al., 2014; Leet et al., 2015; Li et al., 2015; Robinson et al., 2017b). Antibiotics and steroid hormones have been detected in manure and feedyard waste lagoons, (Khan et al., 2008b; Bartelt-Hunt et al., 2012; Zhang et al., 2013; Blackwell et al., 2014) and it is clear that these pharmaceuticals can migrate via land application of manure (Chee-Sanford et al., 2009; Joy et al., 2013; Gall et al., 2014) and groundwater percolation (Bartelt-Hunt et al., 2011; Hafner et al., 2016) into nearby water bodies. The potential for aquatic system contamination is greater in areas where concentrated animal feeding operations are present in high numbers, due to the large volumes of waste and extensive use of pharmaceuticals. In particular, beef cattle feedyards are concentrated in areas of eastern Australia, central United States, central-west Brazil, and Mexico.

Synthetic steroid hormones, a class of veterinary pharmaceuticals used to enhance growth among cattle, have potential to alter reproduction and normal sexual development in exposed wildlife species (Ankley et al., 2003; Jensen et al., 2006; Kidd et al., 2007; Hu et al., 2008; Sellin et al., 2009; Jeffries et al., 2011; Finch et al., 2013;

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Baumann et al., 2014; Jessick et al., 2014; Sangster et al., 2014; Leet et al., 2015; Li et al., 2015; Robinson et al., 2017b). Trenbolone, a synthetic androgen, and estradiol, an endogenous estrogen, are approved for administration in feedyard cattle in many countries; the majority of cattle in US feedyards receive a subcutaneous implant at doses of 200 mg trenbolone acetate and 40 mg estradiol (USDA National Animal Health Monitoring System, 2000; Intervet Inc., 2007). A portion of administered trenbolone acetate is excreted via urine and feces, with 17α-trenbolone and 17α-estradiol as primary metabolites (Blackwell et al., 2014). Melengestrol acetate, a synthetic progestin, is administered to cattle in feed at rates of up to 0.5 mg/head/day (Pharmacia & Upjohn Company, 1994). Administered steroids increase growth, inhibit estrus in heifers, and enhance profitability among beef cattle in feedyards (Lone, 1997).

Antibiotics are used globally in beef cattle feedyards for prophylaxis, growth promotion, and disease treatment (Landers et al., 2012; O'Neill, 2015). Over 15 million kg of antibiotics were administered to livestock animals in the US in 2015 (US Food and Drug Administration, 2015). A variety of antibiotics are approved for use internationally in beef cattle feedyards, with tetracyclines (44%) and ionophores (30%) representing the largest portion of US domestic sales for livestock in 2015 (US Food and Drug Administration, 2015). Ionophores, such as monensin, are not considered medically important for humans and there are no known resistance genes to monensin (Callaway et al., 2003; USFDA Center for Veterinary Medicine, 2003).

β-Adrenergic receptor agonists such as ractopamine are US FDA approved for administration to beef cattle, turkey, and swine. Known as repartitioning agents, these chemicals alter lipid metabolism with an end result of an increased muscle to fat ratio in food animal carcasses (Mersmann, 1998). An estimated 85% of US beef cattle feedyards administer β-agonists as part of their finishing diets, with ractopamine constituting the vast majority of use (Samuelson et al., 2016). Due to concerns about the lack of available data to establish a Maximum Residue Limit, ractopamine use in livestock is banned in over 160 countries such as Russia, China, and the European Union, but is approved for use in the United States, Canada, Australia, and Brazil (European Food Safety Authority, 2009).

Upon entry into aquatic ecosystems, these veterinary pharmaceuticals occur in chemical mixtures, some of which are solubilized whereas others partition into sediments. Individual pharmaceutical concentrations in aquatic systems vary depending on feedyard usage, input source, degree of sorption to soils and sediments, and half-lives in soil and water. Toxicological assessments of aquatic mixtures of veterinary pharmaceuticals are limited, but available data suggests that the toxicity of veterinary pharmaceutical mixtures are generally additive or less than additive (Bona et al., 2014; Białk-Bielińska et al., 2017). However, synergistic effects are possible when pharmaceuticals share a similar mode of action (Eguchi et al., 2004).

Recently, antibiotics, steroid hormones, and the β-agonist ractopamine have been documented in airborne particulate matter (PM) emanating from beef cattle feedyards in semi-arid regions (Blackwell et al., 2015; McEachran et al., 2015; Wooten et al., 2015; Wooten et al., Submitted for publication) and on wildflowers within 1 km of a feedyard (Peterson et al., 2017). Concentrations of the antibiotic monensin were as high as 4600 ng/g in PM immediately downwind of beef cattle feedyards while concentrations of steroids were much lower at a maximum of 60 ng/g. Estimates of total suspended particulates emitted by beef cattle feedyards range from 27 to 127 kg/1000 head/d (Bonifacio et al., 2015). Utilizing current US estimates of 11.0 million head of beef cattle on feed, up to 1.4 million kg of veterinary pharmaceutical-laden airborne PM is generated each day in the United States (USDA National Agriculture Statistics Service, 2017). Up to 90% of airborne PM deposits within 1 km of a beef cattle feedyard (Wooten et al., Unpublished results). The remaining suspended particles, most below 2.5 μm in equivalent aerodynamic diameter, may travel much farther distances before deposition. Airborne PM carrying veterinary pharmaceuticals from beef cattle feedyards may deposit on downwind landscapes, including surface water bodies and their drainage basins. This represents a seldom considered transport mechanism for veterinary pharmaceuticals that holds strong relevance to semi-arid regions with high concentrations of beef cattle feedyards, such as portions of Australia, the United States, Mexico, and Canada.

West Texas, USA, offers an ideal location to assess and characterize this transport phenomenon; high concentrations of beef cattle feedyards are present along with semi-arid climate, high average winds, and flat terrain. Water bodies located in this region almost entirely consist of playa wetlands: shallow, ephemeral basins that fill with surface runoff only after significant localized rainfall. Playa wetlands are discrete hydrologic units on the surface and they do not receive input from other surface water bodies or groundwater (Smith, 2003; Gurdak and Roe, 2009). The only potential sources for veterinary pharmaceuticals are land application of manure within the playa wetland's small basin, or aerial deposition of pharmaceutical-laden PM within the basin. Source apportionment between land application of manure and aerial deposition is difficult, as pharmaceutical concentrations are likely similar between sources and complete land use records are problematic to obtain.

In this investigation, water and sediment samples from playa wetlands near beef cattle feedyards were analyzed for veterinary pharmaceuticals. Ractopamine was analyzed as part of this effort; results for β-agonists have been published separately (Wooten et al., Submitted for publication). This represents the first time playa wetlands have been assessed for feedyard-based veterinary pharmaceuticals and the first evidence possibly linking airborne PM transport of veterinary pharmaceuticals with aquatic systems.

2. Methods

2.1. Sample collection

Playa wetland samples were collected in during a major sampling effort in July 2016 (33 samples) and a very limited sampling window in January 2017 (5 samples) from Deaf Smith County and Castro County, Texas, USA. Sampling counties were selected based on the localized high density of both beef cattle feedyards (in US counties, Deaf Smith is ranked #4 and and Castro is #5 nationally for head of cattle on feed in 2012) (USDA National Agriculture Statistics Service, 2012) and playa wetlands. Wetlands were selected based on proximity to a beef cattle feedyard (within 15 km), accessibility, and availability of surface water. Single grab samples of water and sediment (from the top 10 cm) accessible from the playa wetland edge were stored in glass containers, transported on ice, and frozen at −20 °C until processing. Water and sediment field blanks, consisting of either deionized water or clean sand with deionized water, were passed through decontaminated field equipment and taken at a rate of 1 per day ($n = 9$). Playa water quality parameters (temperature, pH, dissolved oxygen, conductivity, and ammonia) were obtained using a YSI Professional Plus handheld meter (YSI Incorporated, Yellow Springs, Ohio). Water samples were passed through a 1.5 μm glass fiber filter and aliquoted into 200 mL portions. Aliquots of homogenized sediment samples were dried at 40 °C until mass stabilized to obtain percent solids for each sample.

2.2. Steroid extraction

Water samples (200 mL aliquots) were passed through an Oasis HLB solid phase extraction cartridge (6 cc, 200 mg) preconditioned with 5 mL methanol and 5 mL water. Cartridges were dried under vacuum for approximately 30 min and then eluted with 9 mL methanol. Internal standards (d_3-17β-trenbolone and d_5-17β-estradiol) were added and the eluent was dried completely under nitrogen at 35 °C. Extracts were reconstituted with 200 μL of 60% methanol, filtered through at 0.45 μm polyvinylidene fluoride filter, and frozen at −20 °C until analysis via