Sustainable Chemistry and Pharmacy 9 (2018) 76–86

Contents lists available at ScienceDirect

Sustainable Chemistry and Pharmacy

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

Occurrence and fate of antibiotics in manure during manure treatments: A short review

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ARTICLE INFO

Keywords:
Anaerobic digestion
Biogas
Composting
Degradation
Sorption
Transformation products

ABSTRACT

Veterinary antibiotics are frequently applied in livestock farming worldwide and their usage is expected to increase during the next years by more than 60%. The aim of this review is to give a brief overview about excretion rates reported for diverse antibiotics and their fate within different manure treatments. Depending on the substance, < 5% up to 90% of the active ingredient were found to be excreted by the treated organisms leading to antibiotic residues in animal waste. As manure is utilized as substrate in biogas plants, antibiotics can enter this process and might have an effect on biogas and methane yield. This crucial point was subject of several anaerobic digestion studies giving variable results from increased biogas production in only one case (+ 14%) up to almost complete inhibition (− 93%). The fate of antibiotics such as fluoroquinolones, sulfonamides or tetracyclines during manure treatment (anaerobic digestion, storage, composting) was investigated in different setups with composting often resulting in the highest elimination rates (up to > 99%). Based on reported transformation products of distinct antibiotics, degradation cannot be presumed for most compounds. In many cases, only minor structural modifications were observed and several transformation products are still microbiologically active. Consequently, manure treatments should not be evaluated based on the disappearance of the parent compound only. Comprehensive studies should include the elucidation of elimination pathways to identify efficient processes for reducing the input of antibiotics into the environment.

1. Introduction

Increasing incomes in emerging countries have led and will further lead to an increased demand for animal protein. This trend is often accompanied by a shift from extensive to intensive farming systems (Keyzer et al., 2005; Tilman et al., 2011; Van Boeckel et al., 2015). Intensive livestock farming is generally characterized by a higher usage of antibiotics for example due to the application of sub-therapeutic doses as growth promoters. The usage of antibiotics as growth promoters is forbidden within the European Union since 2006 (consolidated text of Regulation EC 1831/2003), but this practice is still employed in other countries (Van Boeckel et al., 2015; Gonzalez Ronquillo and Angeles Hernandez, 2017). Based on estimations, 172 and 148 mg antibiotics are used per kg living or slaughtered animal (population correction unit, PCU) in swine and chicken breeding systems, respectively. This is more than three times the amount that is likely applied in cattle breeding operations (45 mg per PCU) (Van Boeckel et al., 2015). From 2010 to 2030, estimations predict an increase by 67% for the global usage of antibiotics in food animal production and by then, most of the approximately 105,000 t will be applied in China, the USA, Brazil, India and Mexico (Van Boeckel et al., 2015). For the year 2012, the amount of antibiotics used in Chinese poultry and swine production was estimated around 38,500 t of which 23,176 t can be ascribed to sulfonamides, tetracyclines and penicillins (Krishnasamy et al., 2015). In Germany, 742 t antibiotics were distributed to veterinarians in 2016 with 542 t being covered by these three groups (Wallmann et al., 2017). Beside those classes, antimicrobials considered as critically important by the World Health Organization (WHO) are utilized worldwide in veterinary medicine as well (e. g. fluoroquinolones). A short overview of the number of drugs listed for animal use in the U.S. including the classification by the WHO is given by Durso and Cook (2014).

Abbreviations: 4-OH-SDZ, 4-hydroxysulfadiazine; AC, autoclaved; AD, anaerobic digestion; AMO, amoxicillin; B, batch; CIP, ciprofloxacin; CTC, chlortetracycline; DaFX, danofloxacin; DC, doxycycline; DM, dry matter; ENR, enrofloxacin; FW, fresh weight; HRT, hydraulic retention time; (M)IC, (minimal) inhibitory concentration; MICO, micospectone; MR, mixing rate; NOR, norfloxacin; ODM, organic dry matter; OTC, oxytetracycline; PCU, population correction unit; SC, semi-continuous; sim., simulated; SPI, spiramycin; SDZ, sulfadiazine; SMX, sulfamethoxazole; SMZ, sulfamethazine/ sulfadimidine; TC, tetracycline; TMP, trimethoprim; TYL, tylosin

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https://doi.org/10.1016/j.scp.2018.06.004
Received 6 March 2018; Received in revised form 25 June 2018; Accepted 30 June 2018
2352-5541/

Dependent on the structure, antibiotics are only partially absorbed in the animal gut and/or poorly metabolized. Consequently, antibiotics are transferred into liquid manure and feces. Based on data collected from dairy cattle and swine farms in South China, Zhou et al. (2013) calculated excretion masses for antibiotics in China. According to their results, 4.24 and 18.2 mg antibiotics can be excreted by a single cattle and swine per day, respectively, which would correspond to total excretion masses of 164 t respective 3080 t antibiotics in Chinese cattle and swine production per year (Zhou et al., 2013).

As manure is utilized for soil fertilization, antibiotics can consequently be detected in soil samples. Zhang et al. (2016) analyzed soil samples from different protected vegetable farms in China regarding their contents of tetracyclines, sulfonamides and fluoroquinolones. They found contents up to 8400 $\mu g\,kg^{-1}$ for oxytetracycline, though most contents of all compounds investigated were below 100 $\mu g\,kg^{-1}$. For most tetracyclines and fluoroquinolones, detection frequencies of 100% were obtained, whereas sulfonamides were not detected in several samples (Zhang et al., 2016). Sulfonamides show strong sorption to soil particles which cannot be overcome by mild extraction conditions such as extraction at room temperature or ambient pressure (Hamscher et al., 2005; Förster et al., 2008). The presence of sulfonamides in soils, although not frequently detected in soil sample extracts, is proven by the detection of sulfonamides in leachate samples below soils which were amended with contaminated manure (Hamscher et al., 2005; Spielmeyer et al., 2017a). Therefore, antibiotics can enter different environmental compartments where they can persist for many years or even decades. Whether the comparable low concentrations found in the environment might enhance the formation of resistances, is not clarified so far. However, it has been shown that concentrations even below the minimal inhibitory concentration (MIC) can force a selection towards resistant strains (Gullberg et al., 2011).

Several studies deal with the treatment of manure to reduce the content of antibiotics within this matrix. Furthermore, the effect of antibiotics on these treatment processes, mainly formation of biogas during anaerobic fermentation, is investigated. The aim of this short review is to give a general overview about the occurrence of antibiotics in manure as well as their fate during storage, anaerobic fermentation or composting. Furthermore, transformation products reported for manure samples are presented. Publications cited here were (mainly) based on search results in Web of Science obtained for the search string “antibiotic AND manure”. Publications primarily dealing with antibiotic resistance genes were not taken into account. Many studies investigate the occurrence and distribution of antibiotic resistance genes in livestock systems as well as their distribution and impact on the environment (for example Gao et al., 2012; Ji et al., 2012; Zhang et al., 2013; Tang et al., 2015; Beukers et al., 2018; Keen et al., 2018). This aspect is not covered within this article, but the focus is on antibiotics and their fate themselves.

2. Antibiotics in manure

2.1. Excretion rates of selected compounds

For investigation of the excretion (rate) of antibiotics, several studies using ^{14}C-labelled compounds were conducted. Herberg et al. (1978) applied a single dose of ^{14}C-monensin via gelatin capsules to three steers. After 3 days, more than 75% of the radioactivity was recovered in the feces, no excretion occurred via the urine. After 7–11 days, the recovery accounted for 88–102%, of which approximately 50% was estimated to derive from monensin itself (for discussion of transformation products see Section 4) (Donoho et al., 1978; Herberg et al., 1978).

In case of fluoroquinolones, Sukul et al. (2009) used ^{14}C-labelled difloxacin which was given as gelatin capsules to pigs on five consecutive days. Manure was collected for 10 days and 91% of the radioactivity was recovered in these samples with 67.4% being excreted via feces. The majority (96%) of the excreted radioactivity was arriving from difloxacin, resulting in a excretion rate of 88%. Peng et al. (2016) applied ciprofloxacin to layer hens via feed over 5 days. Afterwards they analyzed the manure and found excretion rates between 45% and 52% within 33 days. Enrofloxacin was given to broiler chickens via drinking water for 5 days and the manure was collected for 13 days. Analyses revealed an excretion rate of 74% (Slana et al., 2014). Based on these results it is difficult to estimate whether or not distinct species specific differences concerning the excretion of fluoroquinolones exist as the authors utilized different compounds (difloxacin, ciprofloxacin, enrofloxacin) and different application forms (gelatin capsules, feed, drinking water). These aspects should always be considered when excretion rates of diverse studies are compared.

Lamshöft et al. (2007) gave ^{14}C -labelled sulfadiazine (gelatin capsules) to one pig on four consecutive days. The manure was collected for 10 days and during this time, 96% of the applied radioactivity was detected in the samples. In total, 44% of the applied sulfadiazine was excreted in unaltered form (for discussion of transformation products see Section 4) (Lamshöft et al., 2007). Similar results were reported by Heuer et al. (2008) who used the same setup. Qiu et al. (2016) fed four different sulfonamides (sulfamerazine, sulfachloropyridazine, sulfadimoxine, sulfaquinoxaline) to fattening pigs in two different concentrations over five consecutive days. They collected urine and feces separately for 13 days and analyzed both matrices for their sulfonamide content, but not for metabolites. Both the excretion rate and the partition between urine and feces were structure dependent. The excretion rate increased with decreasing polarity of the respective sulfonamide, resulting in the highest excretion rates for sulfaquinoxaline (85%) and sulfachloropyridazine (62%) (numbers are averages of data provided by Qiu et al. (2016) in Table 5). Sulfadimoxine and sulfamerazine possessed comparable excretion rates (38% and 43%, respectively), but different portions in the urine (57% versus 39%). The highest ratio in the urine was obtained for sulfaquinoxaline (79%) (Qiu et al., 2016). As no metabolites were investigated by the authors, it can only be speculated that different excretion ratios in the urine might be due to unequal metabolism of the respective parent compound.

For tetracyclines, Ince et al. (2013) conducted an onetime injection of oxytetracycline on a dairy cow and they collected the manure over 20 days. Over this time, approximately 20% of the injected oxytetracycline was recovered in the manure. Tetracyclines form stable complexes with metal cations and are incorporated into bones which can lead to a comparable low excretion rate (Clive, 1968; Kühne et al., 2000). Peng et al. (2016) found excretion rates between 83% and 96% for doxycycline given to laying hens (manure collection for 15 days). In contrast to the study by Ince et al. (2013), Peng et al. (2016) applied the antibiotic via feed over 5 days and consequently, their results rather reflect a poor absorption of the compound in the animal gut than species specific differences. In the same study, the authors also investigated amoxicillin, a beta-lactam antibiotic (5 days feeding, 12 days manure collection). Beta-lactams can be easily cleaved under acidic or mild alkaline conditions, but they are more stable under weak acidic or under physiologic conditions (Tsuji et al., 1978). Thus, they can be excreted in considerable amounts, for example between 56% and 68% in laying hens (Peng et al., 2016). Berendsen et al. (2015) and Van den Meersche et al. (2016) reported a reduced stability of amoxicillin and other penicillins in manure, thus, high excretion rates are not reflected by positive results in manure sample analyses (see Section 2.2).

Kuchta and Cessna (2009) conducted a study with weanling pigs that were administered lincomycin (lincosamide) and spectinomycin (aminoglycoside) via feed. The manure was collected from the pit over five weeks. The authors calculated excretion rates of 32% and 3% for lincomycin and spectinomycin, respectively, based on manure sample analysis after five weeks of storage. For their calculation, they assumed that no degradation occurred during that time. However, taking into account results provided by the authors concerning the stability of the compounds in manure (for details see Section 3), excretion rates up to