Bioresource Technology 131 (2013) 476–484

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

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

Degradation of veterinary antibiotics and hormone during broiler manure composting

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HIGHLIGHTS

- Degradation of nine antibiotics and one hormone in 40 days of broiler manure composting.
- More than 99% of target analytes were removed during 40 days of manure composting.
- Target analytes showed short half-life in composting, ranging from 1.3 to 3.8 days.
- Target analytes in composting were affected by pH, temp, TOC, TN, TP and metals.

ARTICLE INFO

Article history:
Received 13 June 2012
Received in revised form 24 December 2012
Accepted 26 December 2012
Available online 11 January 2013

Keywords:
Broiler manure
Veterinary antibiotics
Hormone
Composting
Degradation

ABSTRACT

The fate of nine veterinary antibiotics and one hormone in broiler manure during 40 days of composting was investigated. Results showed that composting can significantly reduce the concentration of veterinary antibiotics and hormone in broiler manure, making application of the post-compost manure safer for soil application. More than 99% of the nine antibiotics and one hormone involved in this study were removed from the manure during 40 days of composting. The target antibiotics and hormone showed short half-life in broiler manure composting, ranging from 1.3 to 3.8 days. The relationship between the physico-chemical properties of soil, manure and manure compost and its veterinary antibiotic and hormone concentration was statistically evaluated by Pearson correlation matrix. The concentration of veterinary antibiotics and hormone in manure compost was suggested to be affected by physico-chemical properties such as pH, temperature, total organic carbon (TOC), total nitrogen (TN), total phosphorus (TP) and metal contents.

1. Introduction

Recently, numerous researchers have detected a wide range of antibiotic residues in aquatic and terrestrial environments (Karcı and Balcıoğlu, 2009; Martínez-Carballo et al., 2007; Tamtam et al., 2008; Zou et al., 2011). These pharmaceuticals mainly originate from either human pharmaceuticals entering the environment via wastewater treatment plants or from veterinary antibiotics entering the environment via application of animal manures (Kim et al., 2011). A large quantity of animal manure is produced yearly as a by-product from the concentrated animal feeding operations (CAFOs) and is subsequently applied on agricultural soil as fertilizer, making it one of the main sources of terrestrial pharmaceutical pollution. The occurrences of antibiotics in soil and manure have been reported by previous researchers (Aust et al., 2008; Karcı and Balcıoğlu, 2009; Martínez-Carballo et al., 2007). The release of antibiotics and hormones into the environment is of concern because the persistency of these compounds may lead to the development of antibiotic-resistant bacteria (Heuer et al., 2008; Hoa et al., 2011; Sengeløv et al., 2003) and are potential endocrine disrupting compounds (EDCs) (Lange et al., 2002).

There is limited information on antibiotics and hormones degradation that occurs during manure composting, especially the effects of composting of multiple classes of antibiotics and hormones which represent the actual situation in CAFOs. In most of the related studies, only single compound was evaluated in each of the composting experiments (Arikan et al., 2009, 2007; Bao et al., 2009; Ramaswamy et al., 2010). This includes a study by Ramaswamy et al. (2010), the study showed that the concentrations of salinomycin in poultry manure decreased by 99% during 38 days of

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http://dx.doi.org/10.1016/j.biortech.2012.12.194

composting. In the same way, the degradation of oxytetracycline was evaluated in therapeutically-treated beef calves manure composting (Arikan et al., 2007), the concentration of oxytetracycline displayed a 95% reduction after 35 days of composting. Again, another similar study was done by Bao et al. (2009) to determine the effects of composting in aged and spiked manures on the depletion of chlortetracycline. At the end of composting, more than 90% of chlortetracycline in the broiler and layer hen manure composting (42 days) was depleted except for hog manure composting, with a removal of only 27%. On the other hand, the effects of composting in reducing multiple classes antibiotics that were evaluated in Dolliver et al. (2008) is closer to actual CAFOs practice where more than one antibiotic was prescribed to the animals. In that particular study, concentrations of chlortetracycline declined rapidly during composting (>99%), whereas concentrations of monensin and tylosin declined gradually (54% to 76%) and there was no degradation of sulfamethazine in 35 days of turkey litter composting.

Instead of developing technologies to assist the degradation of antibiotics in soil and prevent them from contaminating surface and ground water, a more effective and practical solution was found to reduce environmental contamination from veterinary antibiotics. It is more effective to eliminate the antibiotics in the manure before it is applied to agricultural land as fertilizer (Ramaswamy et al., 2010) and the positive effects of composting were reported by many previous literatures as described above. On-farm manure management strategies, such as composting, may provide a practical and economical solution for reducing the risk of pharmaceutical pollution in the environment. Thus, the objective of this study is to evaluate the efficiency of laboratory scale composting in reducing nine veterinary antibiotics and one hormone in broiler manure by using LC–MS/MS. Multiple classes of antibiotics and hormone were evaluated in this study due to the fact that at least seven of these compounds were detected in broiler manure samples before land application (Ho, 2012) (unpublished data). Detailed information of the individual target analytes, covering chemical structure, chemical abstract service (CAS) number, antibiotic class, molecular weight, octanol–water partition coefficient and pK_a are summarized in Table 1.

2. Methods

2.1. Chemicals and standards

The reference standards doxycycline hyclate ⩾99%, erythromycin ⩾850 μg/mg potency, progesterone 99.1% and tylosin tartrate ⩾95% were obtained from Sigma–Aldrich (Germany). Amoxicillin 98.2%, norfloxacin ⩾98%, sulfadiazine 99.8% and trimethoprim 99.3% were purchased from LKT Laboratories, Inc. (USA). Enrofloxacin 99%, flumequine 98% and tilmicosin 98.5% were purchased from Dr. Ehrenstorfer (Germany). The isotope internal standards $^{13}C_3$-trimethoprim, $^{13}C_2$-erythromycin, $^{13}C_6$-sulfamethazine, $^{13}C_6$-thiabendazole were purchased from Cambridge Isotope Laboratories, Inc. (MA, USA) and ciprofloxacin-d_8 hydrochloride 99% was purchased from Dr. Ehrenstorfer (Germany). Individual stock standard solutions (1000 mg/L) were prepared monthly by dissolving the reference standards in an appropriate solvent according to Ho et al. (2012), and working standard solutions (10 mg/L) were prepared from the stock solution weekly.

2.2. Collection of broiler manure

In this experiment, broiler manure sample was collected from large-scale broiler farm from Linggi, Negeri Sembilan (N2°27′ 34.47″, E101°59′07.74″). Roughly 30 kg composite broiler manure samples were obtained in total from different points of the farm. The broiler chicken manures were composted immediately after 1 day of collection.

2.3. Composting experimental design

The manure composting experiment was conducted in triplicate samples by using three identical 12 L plastic containers. Each plastic container contained 5 kg dry weight (DW) of manure material.

Despite the existence of residual antibiotics and hormone in broiler manure, an additional of 5 mg/kg DW of the target analytes (doxycycline, enrofloxacin, erythromycin, flumequine, norfloxacin, sulfadiazine, tilmicosin, trimethoprim, tylosin and progesterone) were spiked into each replicate of the sample. The initial concentration of each analyte in broiler manure before spiking is provided in the Supplementary material at Elsevier Publisher Website. Throughout the composting process, the moisture content of the manure in each container was kept at 50–60% for optimum composting. Manure moisture content was controlled at 1-day intervals by adding enough water to obtain constant moisture content throughout the composting process. To prevent moisture loss, the composts were covered with hay. The plastic covers of the containers were drilled with small holes to allow aeration and prevent moisture lost. For aeration, the composts were turned and mixed at 1-day intervals during the 40 days of composting in order to ensure an oxygen supply to maintain aerobic conditions of the materials. The experiment was conducted at the mean ambient temperature of 28 to 33 °C in an open laboratory. Samples for analysis were taken from each manure composting test at days 0, 2, 4, 6, 9, 13, 18, 24, 30 and 40 of composting for determination of antibiotics and hormone concentrations. The compost samples were stored at −20 °C if it was not possible to analyze immediately. All analyses were completed within 1 week of sampling. Table 2 shows the characteristics of raw materials for broiler manure composting.

2.4. Determination of physico-chemical properties of manure compost samples

Composts pH, electrical conductivity (EC), total organic carbon (TOC), total nitrogen (TN), total potassium (TK), total phosphorus (TP), C/N ratio, Cr, Cu, Pb, Ni, Zn, Fe, Cd, Na, Ca, and Mg content were measured at days 0, 2, 4, 6, 9, 13, 18, 24, 30 and 40 of composting.

Compost pH and EC were determined in soil:distilled water (1:1) suspension using Thermo Orion 3-star pH-meter (CA, USA) (Zhang and Fang, 2007) and YSI 30 handheld conductivity meter (OH, USA) respectively. The analysis of TN, C/N ratio and TOC on the manure and soil was analyzed by using Elemental vario MACRO CHNS/O analyzer (Germany). TK, TP, Na, Mg, Ca, Cr, Cu, Pb, Ni, Zn, Fe and Cd in composts were microwave acid digested by Multiwave 3000 (PerkinElmer, USA) by using the method as described in Melaku et al. (2005). The extracts were then analyzed by ICP-MS (PerkinElmer, USA).

2.5. Sample pretreatment, extraction and SPE

The target veterinary antibiotics and hormone in compost samples were extracted and analyzed using the method described by Ho et al. (2012). Briefly, 1 g wet weight of solids was extracted with 5 mL of extraction buffer (MeOH:ACN:0.1 M EDTA:McIlvaine buffer (pH 4), 30:20:25:25). The mixture was vortex mixed for 30 s and then placed into an ultrasonic bath for 10 min. The tube was centrifuged at 4000 rpm for 10 min. The supernatant was then decanted into a clean 500 mL plastic bottle and the settled solid was extracted twice more, and a total of 20 mL of supernatant was then