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Chemical and biological assessment of endocrine disrupting chemicals in a full scale dairy manure anaerobic digester with thermal pretreatment

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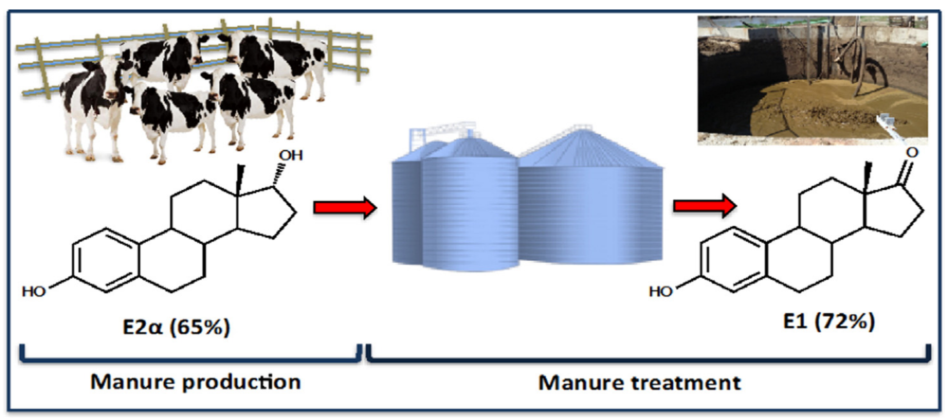
HIGHLIGHTS

- Dairy manure contains natural estrogens known as potent endocrine disruptors
- Estrogen transformation was evaluated through a full-scale anaerobic co-digestion system.
- E1 was the dominant estrogen form found in the digestate and the main contributor to estrogenicity.
- Mesophilic anaerobic digestion did not change total estrogen concentrations significantly.

GRAPHICAL ABSTRACT



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ABSTRACT

Concentrated animal feeding operations are important sources of estrogens and their conjugates, which are introduced into the environment through manure land application. In this study, concentrations of estrogens were measured in an anaerobic co-digestion system with thermal pasteurization pretreatment. Free estrogens (estrone (E1), 17α-estradiol (E2α), 17β-estradiol (E2β), estriol (E3)) were analyzed by gas chromatography with mass spectrometry (GC/MS), and conjugated estrogens (sulfate- and glucuronide-conjugates) were analyzed by liquid chromatography with tandem mass spectrometry (LC/MS/MS). Additionally, yeast estrogen screen assay was used to determine the estrogenic potential of the manure. The total hormone concentrations (mainly E1, E2α, E2β, and sulfated estrogens) were observed at concentrations up to a total of 7100 ng/L in the liquid fraction, while free estrogen levels were 630 ng/kg in the solid fraction of the untreated manure. The total hormone concentration did not decrease significantly during digestion, however, the relative composition of the estrogens changed from E2α (65%) being the predominant species before digestion to mostly E1 (72%) after digestion. This conversion process has important implications because E1 is more estrogenic than E2α. Total E2 equivalents associated with E1, E2α and E2β concentrations as determined by GC/MS indicate that E1 is the most important contributor to the endocrine-disruption activity of the treated manure.

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1. Introduction

The application of animal manure as a natural fertilizer is a common practice in the United States (US). However, there has been an increasing concern regarding this practice because manure contains natural estrogen hormones (Combalbert et al., 2012; Hutchins et al., 2007) that are known endocrine disrupting chemicals (EDCs) in the environment (Desbrow et al., 1998). EDCs can affect aquatic and wildlife species at low concentrations (ng/L) (Jobling et al., 2006). Dairy concentrated animal feeding operations have been identified as an important source for the release of natural estrogens in the environment (Hutchins et al., 2007; Kolodziej et al., 2004; Zheng et al., 2008). Estrogens [estrone (E1), 17α-estradiol (E2α), 17β-estradiol (E2β), and estriol (E3)] and their conjugates (glucuronide and/or sulfate groups) are naturally produced by cattle, and are excreted in urine and feces (Hanselman et al., 2003). Among these hormones, E2β exhibits the highest estrogenic activity, while the conjugated forms are considered non-estrogenic (Combalbert et al., 2012; Hutchins et al., 2007; Singh et al., 2013).

The US government regulations require livestock farms to implement manure storage and treatment systems to control pathogens, odor, and nutrient loading in the environment (Burke and Dennis, 2001; Ogejo, 2009). The major federal law affecting manure management on animal operations is the Clean Water Act, through the National Pollutant Discharge Elimination System program (USDA, 2001). Conventional manure handling on US dairy farms consists of either daily spread of manure or long-term storage. More advanced manure treatments include solid–liquid separation, anaerobic lagoons, and anaerobic digesters, among others (San Joaquin Valley Dairy Manure Technology Feasibility Assessment Panel, 2005; Zhao et al., 2007). Solid–liquid separation of manure involves sedimentation or mechanical methods to facilitate ease of pumping long distances, and harvesting of solids for use as cow stall bedding (San Joaquin Valley Dairy Manure Technology Feasibility Assessment Panel, 2005). Both anaerobic lagoons and anaerobic digesters rely on anaerobic bacteria to break down organic matter in an oxygen-free environment (Chastain and Henry, 2015). Anaerobic digesters are sophisticated systems with temperature control, pre- and post-treatment of the manure, shorter hydraulic times than anaerobic lagoons and biogas collection (Bernet and Béline, 2009). Anaerobic digesters are increasingly used as a sustainable option for animal waste management (Bidart et al., 2014). In fact, the US Department of Agriculture will support the construction of 500 new digesters in dairy cattle and hog operations over the next 10 years to increase energy generation as part of their focus on climate-smart agriculture (USDA, 2015).

It is estimated that the US dairy cattle industry contributes nearly 90% of the annual estrogen excretion by farm animals (Lange et al., 2002). Nonetheless, studies available on estrogens in dairy manure are limited. The concentrations of estrogens in manure can be affected by the different treatment systems applied (Raman et al., 2004). In systems such as successive lagoons (Hutchins et al., 2007; Zheng et al., 2008) and advanced lagoon systems (Gadd et al., 2010a) estrogen concentrations have been shown to decrease during treatment. Little is known about the fate of hormones and the endocrine-disrupting potential of manure in anaerobic digesters, especially under industrial farm-scale operations. There is one study that examined the changes in the estrogen levels in dairy manure under a farm-scale anaerobic digestion system, which reported a 14.7% removal efficiency of the total estrogens (free and conjugated forms of E2β and E1) (Zhang et al., 2014). Nonetheless, E2α was not measured in the study despite the fact that it is the major form of estrogen excreted by cattle (Hanselman et al., 2003; Zheng et al., 2008). Because E2α is present in much higher levels than E2β, it can be an important contributor to the estrogenic potential of dairy manure and should not be ignored (Gadd et al., 2010b). Removal of estrogens in swine manure by anaerobic digestion has been previously investigated (Rodriguez-Navas et al., 2013; Suzuki et al., 2009; Zhang et al., 2014). However, the estrogen profile in manure excreta differs between livestock species; E1 and E3 are major estrogen forms in swine manure (Furuichi et al., 2006), E1 and E2β in poultry manure, while cattle manure is known to be richer in E2α (Hanselman et al., 2003).

This study provides a general assessment of estrogen levels and evaluates the endocrine disrupting potential of dairy manure through an anaerobic digestion system. This system uses pasteurization pretreatment and co-digestion of raw manure with food waste substrates. Pasteurization pre-treatment facilitates disintegration of cell membranes through progressive lysis as temperature is increased, resulting in solubilization of organic compounds (Ariunbaatar et al., 2014). To our knowledge, this is the first study that provides data regarding the transformations of estrogen hormones and the endocrine disrupting potential of dairy manure in a full-scale manure treatment system that employs pasteurization and anaerobic co-digestion process.

2. Materials and methods

2.1. Sample collection

Manure samples were collected from a dairy farm located in Western New York. This farm has 2200 dairy cows and supplies the manure to an advanced digestion facility. This facility includes a pasteurization step (67 °C, 1 h), followed by a 22-day mesophilic anaerobic digestion process. Detailed description about the farm and its waste treatment operation system is given in supplementary data.

Samples were collected from three sampling locations within the system: (1) before pasteurization (raw manure), (2) after pasteurization (mixture of raw manure and food waste), and (3) after anaerobic digestion (digestate). A diagram of the waste disposal system, and sampling locations is shown in Fig. 1.

Preliminary samples were collected in the winter (January 2013) for methods development and to inform the design of future sample collection. Data from preliminary samples are presented in supplementary data (Fig. S1). Additional sampling took place in the spring (April 2013). Raw manure and post pasteurization samples were collected during 3 consecutive days. Post digestion samples were collected at 2, 3, and 22 days after the first samples were collected from the raw manure tank and after pasteurization. The reason for collecting during these days was to demonstrate that the composition of the manure in the anaerobic digestion system is maintained within the 22-day average hydraulic retention time.

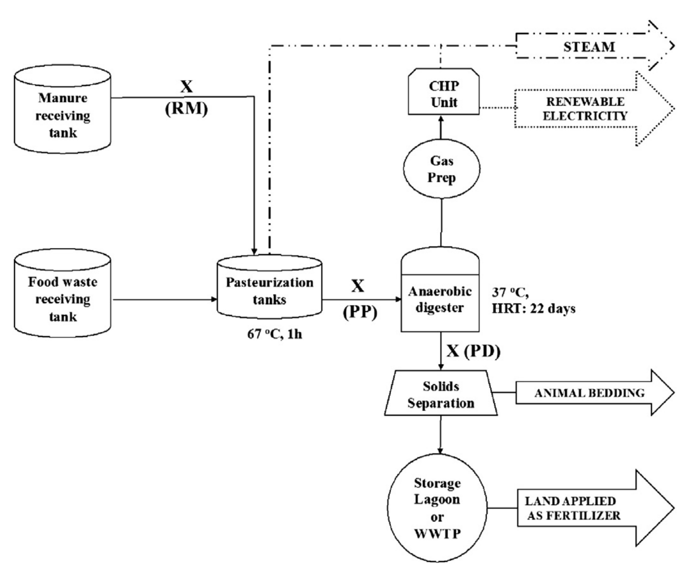

Fig. 1. Schematic diagram showing the complete mixed-waste anaerobic digester investigated in this study. Sampling points are marked with X (RM = Raw manure, PP = Post pasteurization, PD = Post digestion). HRT = Hydraulic retention time.