Science of the Total Environment 538 (2015) 423–430

Contents lists available at ScienceDirect

Science of the Total Environment

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

Accumulation of steroid hormones in soil and its adjacent aquatic environment from a typical intensive vegetable cultivation of North China

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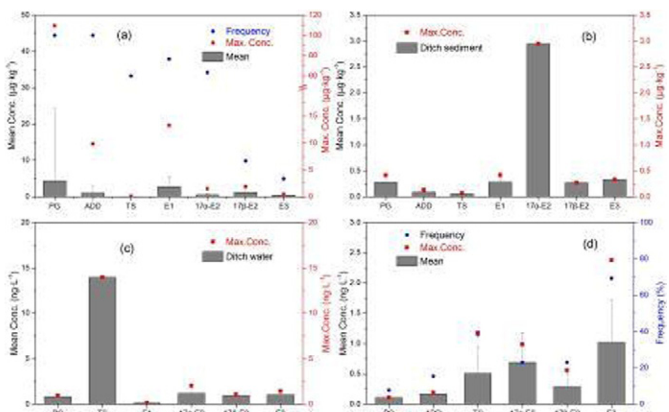
HIGHLIGHTS

- Seven steroids were detected in soil and adjacent drainage ditch sediment.
- Six steroids were found in drainage ditch water and groundwater.
- Progesterone, androstendione and estrone accumulated relatively easily in soils.
- Testosterone and estriol were easily leached to groundwater.
- Concentrations of steroids in soil and groundwater were highly spatially variable.

GRAPHICAL ABSTRACT

Accumulation of steroid hormones in (a) greenhouse soil, (b) ditch sediment, (c) ditch water and (d) groundwater.



ARTICLE INFO

Article history:
Received 11 June 2015
Received in revised form 12 August 2015
Accepted 12 August 2015
Available online 25 August 2015

Editor: Adrian Covaci

Keywords:
Poultry litter
Agricultural application
Steroid hormone
Residue

ABSTRACT

Steroid hormones released from manure agricultural application are a matter of global concern. The residual levels of steroid hormones were studied in a typical intensive vegetable cultivation area in northeast China, with a long history of heavy manure application. Seven steroids (estrone, 17α-estradiol, 17β-estradiol, estriol, testosterone, androstendione and progesterone) were analyzed from soil sampled from vegetable greenhouses, from sediments and water from the adjacent drainage ditch and from the groundwater. The results showed that target steroids were detected in the soil samples, with detection frequencies varying from 3.13 to 100%. The steroid concentrations varied substantially in soils, ranging from below the detection limit to 109.7 $\mu g \cdot kg^{-1}$. Three steroids—progesterone, androstendione and estrone—were found to have relatively high residue concentrations in soil, with maximum concentrations of 109.7, 9.83 and 13.30 $\mu g \cdot kg^{-1}$, respectively. In adjacent groundwater, all the steroids, with the exception of estrone, were detected in one or more of the 13 groundwater samples. The concentrations of steroids in groundwater ranged from below the method detection limit to 2.38 $ng \cdot L^{-1}$. Six of the seven (excluding androstendione) were detected in drainage ditch water samples, with concentrations ranging from below the detection limit to 14 $ng \cdot L^{-1}$. Progesterone, androstendione and estrone accumulated relatively easily in soils; their concentrations in groundwater were lower than those of other steroids. The concentrations of testosterone and estriol were relatively low in soil, while in groundwater were higher than those of other steroids. The residual levels of steroids in soil and groundwater showed a clear spatial variation in the

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http://dx.doi.org/10.1016/j.scitotenv.2015.08.067

study area. The residual levels of steroid hormones in soil varied substantially between differently planted greenhouses.

1. Introduction

Natural steroid hormones have received considerable attention because of their endocrine-disrupting effects on aquatic organisms (Orlando et al., 2004; Alvarez et al., 2013). Environmentally-relevant concentrations of estrogen hormones in aquatic environments have been found sufficient to stimulate production of a female protein in male fish, with no effect concentrations for 17β-estradiol of 1–10 $ng\cdot L^{-1}$ (Routledge et al., 1998). Livestock manure is accepted as an important source of these compounds with major inputs to the environment (Shore and Shemesh, 2003; Lorenzen et al., 2004; Bevacqua et al., 2011). Natural estrogens were detected in various types of animal wastes, such as 17β-estradiol content of between 14 and 904 $mg\cdot kg^{-1}$ in poultry litter (Gall et al., 2011; Hanselman et al., 2003). Luo et al. (2013) reported that estrogen content, including estrone, 17α-estradiol, 17β-estradiol and estriol in water and sediments, increased within a watershed that was subject to animal manure application. Animal manures contain more androgens and gestagens than estrogen hormones (Shore and Shemesh, 2003). It has been suggested that testosterone can suppress the antibody-forming cell responses in Chinook salmon (Slater and Schreck, 1993). Shore et al. (2004) showed that testosterone accumulated in a watershed originated from washout of cattle pasture. Progesterone is also frequently detected in waste storage lagoons and shed effluents and could be potentially hazardous to the environment (Gadd et al., 2010; Liu et al., 2012).

Manure-borne hormones can be transported to surface water through runoff produced by rainfall or irrigation. Mimic rainfall experiments have confirmed that animal manure application increases concentrations of steroid hormones in runoff (Kolodziej and Sedlak, 2007; Jenkins et al., 2009; Gall et al., 2011; DeLaune and Moore, 2013). For example, high (up to 58 ng L^{-1}) estrone concentrations were measured shortly after applications of manure in a small agricultural watershed (Lafrance and Caron, 2013). Manure type, application rate, and time until the first runoff event occurs after manure application will affect the transport of steroid hormones to surface water (DeLaune and Moore, 2013). Such research was only concerned with the risk of manure steroids entering surface water from animal manure applications directly (Gadd et al., 2010; Liu et al., 2012; Yost, et al., 2014; Bartelt-Hunt et al., 2012; Gall et al., 2011). Residues of steroids in animal manure can also leach through soil into the groundwater. Groundwater underlying livestock wastewater impoundments has also been shown to contain natural steroid hormones (Arnon et al., 2008; Bartelt-Hunt et al., 2011). To our knowledge, there has been little investigation into the occurrence of steroid hormones in groundwater associated with animal manure agricultural application.

Long-term animal manure application will increase pollutant accumulation in agricultural soils, including heavy metals and antibiotic compounds (Li et al., 2015a,b). Recent research indicated that estrogen in pig slurry redistributed in soils and remained present in the soil for 46 days (Mostofa Amin et al., 2014). Experiments confirmed that steroid hormones entering agricultural soil could be assimilated by lettuce and maize and might represent a human health risk (Card et al., 2013; Shargil et al., 2015). China's economic boom in recent decades has stimulated demand for non-seasonal vegetable products that has consequently led to a vast expansion of vegetable production. To improve vegetable production, much more animal manure has been applied to vegetable greenhouses than to grain cropland (Li et al., 2014). However, most of the livestock and poultry feces contain antibiotic residues and estrogens and are applied to soil without effective treatment (Hu et al., 2010; Zhang et al., 2014). Our previous study showed that the soil might be contaminated by antibiotic residues from chicken manure in Shouguang, which has the largest vegetable cultivation base in north China (Li et al., 2014).

The objectives of this study were to investigate the occurrence and concentration of steroids in soils, drainage ditch water, sediments and groundwater in the vegetable production base in Shouguang; to explore the spatial pattern of steroids in soils and groundwater; and to analyze the differences in steroid distribution between soil, water and sediment.

2. Materials and methods

2.1. Study area

The study area was a typical intensive vegetable cultivation region in Shouguang, Shandong Province, northeast China. The study region covers an area of about 160 km^2. The region has a warm, temperate, continental monsoon climate with seasonal changes (e.g., hot and rainy in summer; cold and dry in winter). The annual average temperature is 12.7 °C and the hottest and coldest months are June and January, with monthly average temperatures of 26.5 °C and −3.1 °C, respectively. The annual precipitation is about 593.8 mm, and rainfall is most frequent in June, July, and August.

Shouguang, located in Shandong Province, is the major vegetable production base in northern China, with several hundred years of cultivation history and 25 years of vegetable cultivation using greenhouses. The vegetables are grown in large greenhouses between 500 and 1000 m^2 in area. The primary vegetables grown in the region are cucumbers, tomatoes, peppers, melons, and eggplant. Vegetables are cultivated in 2–3 crop cycles per year, and are fertilized in autumn or winter, 1–2 times per year. Animal manure, such as chicken manure and cow dung, has been used as organic fertilizer for several years, and is mainly sourced from the local livestock and poultry farms of the surrounding counties. The annual manure application quantity ranged from 1.3 to 17.1 $kg\cdot m^{-2}$.

2.2. Sampling

Sampling was performed in October, 2013. The soils and adjacent ditch water, sediments, and underground water were sampled for analysis of seven types of target steroid hormones, including estrone (E1), 17α-estradiol (17α-E2), 17β-estradiol (17β-E2), estriol (E3), androstendione (ADD), testosterone (TS) and progesterone (PG). A total of 32 surface soil samples, including 30 greenhouse soils and two non-greenhouse soils, were collected. The greenhouse soils were sampled from seven types of greenhouse plots; cucumber, pepper, eggplant, luffa, melon, tomato and coriander (Fig. 1). Each surface soil sample was collected from one vegetable greenhouse. Using a small shovel, soil samples were collected from 0–15 cm below the soil surface. Five sampling sites were distributed along an S-shaped path within each greenhouse, then fully mixed to form a single composite sample. 3 Surface water samples and 3 sediment samples were taken from the drainage ditches adjacent to the greenhouses. Surface water samples were collected at 0–1 m overlying water depths. Sodium azide was added to the water samples at 200 $mg\cdot L^{-1}$. The surface sediment samples (5-cm depth) were collected using a grab sampler. A total of 13 groundwater samples were collected from irrigation wells that were usually within 100 m of the greenhouses. All samples were transported to the laboratory within 7 h of collection; the water samples were immediately analyzed once transported to the laboratory and soil and sediment samples were stored at −20 °C for further extraction and analysis.