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## Fate of tetracyclines in swine manure of three selected swine farms in China

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### Abstract

Veterinary antibiotics can enter the environment due to the common practice of land application of manure from treated animals. The environmental fate of tetracyclines in swine manure after composting and field application remains largely unknown. This study analyzed the concentrations of tetracyclines in manure, manure-based compost and compost amended soil in selected swine farms from Beijing, Jiaxing and Putian, China to determine the dilution effects of antibiotics when released into the soil environment. The results demonstrate that residues of antibiotics were detected in all samples and chlortetracycline as well as its degradation products should be regarded critically concerning their potential ecotoxicity. Application of manure-based compost to soil could reduce the possible risk posed by antibiotic contamination, but the trigger value of 100 µg/kg was still exceeded in soil samples (776.1 µg/kg dw) from Putian City after application of compost. Field studies such as the present one can help to improve the routine administration of antibiotic-containing composted manure.

**Key words:** tetracyclines; swine manure; compost; soil; environmental fate

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### Introduction

Swine production is globally distributed and a majority of the production occurs in China. Nowadays, the swine production is becoming more specialized, concentrated and industrialized (Chen, 2009). Consequently, large amounts of swine manure are produced and the environmental concerns about manure disposal are increasing (Martinez et al., 2009). Traditionally, swine manure is directly applied to farmland in China. Since swine manure is nutrient-rich, it can greatly decrease commercial fertilizer costs if properly used. Application of raw manure to farmland can contribute ammonia, pathogens, and volatile organic compounds. Many studies have explored composting as an alternative to direct land application of livestock waste (Gil et al., 2008). It is a well-developed waste management practice whereby the organic components of raw manures are biologically decomposed and the pathogens are destroyed under controlled conditions (U.S. Composting Council, 2001). The composted manure is odorless, fine-textured and has low moisture content, volume and weight. It can be easily handled, stored or applied to land as a soil amendment.

On the other hand, antibiotics are widely used in swine feeds for growth promotion and disease treatment or pre-

vention (Bao et al., 2009; Kemper, 2008). Many antibiotics are poorly absorbed in the animal tissues, and subsequently could be excreted in the form of their parent compounds or metabolites to manure (Thiele-Bruhn, 2003). After repeated manure application, antibiotics tend to persist and accumulate in soils. Residual antibiotics may exert a selective pressure on soil microorganisms and alter the composition of the soil microbial community, contributing to the spread of antibiotic-resistant bacteria or resistance genes (Boxall et al., 2003; Schmitt et al., 2006; Yang et al., 2009). Therefore, it is necessary and important to treat and dispose of animal manure before its land application to reduce the amount of veterinary antibiotics released into the environment and minimize the risk of the widespread development of resistant bacteria derived from residual antibiotics (Kumar et al., 2005). Composting has been proved to be a feasible and effective approach to promote removal of antibiotics in animal manure (Arikan et al., 2007; Dolliver et al., 2008; Ramaswamy et al., 2010). But currently, manure-based compost from swine farms has not been well characterized. Most of the studies were carried out at the laboratory scale and only focused on the removal of parent antibiotics (Li et al., 2010; Sharma et al., 2009).

Tetracyclines (TCs) are the most commonly used antimicrobials in swine production. Residues of the tetracycline class of antibiotics in swine manure have been

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widely reported (Aust et al., 2008; Watanabe et al., 2010; Pan et al., 2011). However, few field studies on levels of veterinary antibiotics in soil after amending with manure compost have been published (Kwon, 2011). The objective of this study is to understand the occurrence and the fate of TCs and their degradation products in swine manure after composting and field application. The results could provide useful information for assessing the impacts or potential risks of antibiotics to ecosystems and for proper handling of antibiotic-containing manure.

## 1 Materials and methods

### 1.1 Sample collection

Three representative swine farms from Beijing, Jiading (Zhejiang Province) and Putian (Fujian Province) were selected as sampling sites and a total of 36 samples were collected in September 2010. These large-scale swine farms (producing 10,000 market hogs per year) have developed modern compost systems to produce organic fertilizer with swine manure and other sources of carbon. Agronomic plots were also established near the swine production units. Four replicates of raw manure and manure-based compost were taken from the manure or compost heaps stockpiled in each plant and random soil samples were collected from the plots upon which manure-based compost had been applied. All the samples were kept on dry ice before being transferred to the laboratory and stored at  $-80^{\circ}\text{C}$  until analysis.

### 1.2 Sample pre-treatment

Extraction of TCs from the solid samples was based on the method developed by Karci and Balcioglu (2009) with minor modification. Briefly, the samples were freeze-dried to complete dryness and sieved through a 60-mesh sieve before further handling. After transferring 3.0 g of soil/compost or 1.0 g of manure into a centrifuge tube, 20 mL McIlvaine- $\text{Na}_2\text{EDTA}$  extraction buffer was added into each tube and the centrifuge tubes were vortexed for 30 sec. The samples were sonicated in an ultrasonic bath (KQ-600DE, Kunsan, China) for 10 min and then centrifuged at 4000 r/min for 15 min. The supernatant was decanted into a new glass bottle and extraction was repeated twice. The extracts were combined and filtered through glass fiber filters. Then the samples were preconcentrated and cleaned-up by solid phase extraction (SPE) cartridges (Oasis HLB, 6 cc/500 mg). The HLB cartridges were preconditioned with 5 mL methylene chloride, 5 mL of methanol and 5 mL of McIlvaine- $\text{Na}_2\text{EDTA}$  buffer. After the extracts were loaded, the cartridges were rinsed with 6 mL of ultra pure water and then eluted with 5 mL of methanol. The eluates were concentrated to dryness under a gentle nitrogen flow and then dissolved in 0.5 mL of methanol. Before LC-MS-MS analysis the methanol extracts were diluted 1:1 (V/V) with Millipore water. Recoveries were determined by spiking a mixture of standards into the three matrices (manure, compost and soil) at the concentrations of 400  $\mu\text{g/kg}$  TCs, followed by the same extraction procedure

described above. Samples were analysed in triplicate.

### 1.3 Sample analysis

A Waters ACQUITY UPLC<sup>TM</sup> system (USA) equipped with a Waters Micromass Quattro Premier XE (triple-quadrupole) detector was used to separate and quantify antibiotic samples as described by Jia et al. (2009). Five target TCs, including tetracycline (TC, 95%), oxytetracycline (OTC, 95%), chlortetracycline (CTC, 80%), doxycycline (DXC, 98%), and methacycline (MTC), and ten degradation products, including 4-epitetracycline (ETC), anhydrotetracycline (ATC), 4-epianhydrotetracycline (EATC, 97%), 4-epioxytetracycline (EOTC, 97%),  $\alpha$ -apo-oxytetracycline ( $\alpha$ -apo-OTC),  $\beta$ -apo-oxytetracycline ( $\beta$ -apo-OTC), isochlortetracycline (ICTC, 97%), 4-epi-chlortetracycline (ECTC, 97%), anhydrochlortetracycline (ACTC), and 4-epi-anhydrochlortetracycline (EACTC) were analyzed (Wu et al., 2010). The five TCs were obtained from Sigma-Aldrich (USA), and the ten degradation products were purchased from Acros Organics (Geel, Belgium). The instrument detection limits ranged from 0.03 to 0.10  $\mu\text{g/L}$ . Average recoveries of TCs ranged from  $(32\pm 11)\%$  to  $(87\pm 6)\%$  for all the samples. Satisfactory recoveries were observed for the parent compounds such as OTC, CTC and TC, but recoveries of degradation products were relatively low. The recoveries were usually in the same range as for other published methods (Hamscher et al., 2002; Martínez-Carballo et al., 2007; Tylová et al., 2010). The antibiotic concentrations were not corrected for recoveries.

### 1.4 Characterization of manure, compost and soil samples

Samples were characterized using different parameters to obtain a comprehensive data set for the samples. The pH and electrical conductivity (EC) were determined from a sample:water (1:5, W/V) suspension using a pH meter (FE20, Mettler Toledo, Swiss) and EC meter (SenION156, HACH, USA). The organic matter and total-P were analyzed according to the standard methods (Bao, 2000). Total-N and total-C were determined using an elemental analyzer (Vario EL III, Elementar, Germany). The physicochemical properties of the swine manure, manure-based compost and compost-amended soil are summarized in Table 1.

## 2 Results and discussion

### 2.1 Occurrence of tetracyclines in manure

The tetracycline class of antibiotics was commonly detected in the swine manure samples analyzed (Table 2), indicating that these compounds had been fed to the animals. However, the concentration of antibiotics varied greatly for manure in different regions. The highest total concentration of TCs was up to 15264.0  $\mu\text{g/kg}$  dw for manure sampled from Putian and the lowest concentration was only 117.1  $\mu\text{g/kg}$  dw for manure sampled from

**Table 1** Basic physicochemical properties of the samples

Sample	pH	OM (%)	EC (mS/cm)	TN (g/kg)	TP (g/kg)	C/N ratio
BJM	6.53	55.7	14.46	2.49	10.58	10.69
JXM	7.25	67.1	11.04	3.44	18.25	9.57
PTM	6.48	78.2	8.45	4.42	23.75	8.85
BJC	8.07	25.3	3.83	1.33	14.84	12.48
JXC	7.46	53.4	10.17	2.76	37.61	8.74
PTC	7.53	42.1	6.95	1.70	13.24	13.78
BJS	8.15	11.4	0.38	5.12	5.42	10.94
JXS	7.58	5.1	0.24	2.24	3.62	7.38
PTS	6.86	6.2	0.54	1.82	2.29	5.58

BJM: Beijing manure; JXM: Jiaxing manure; PTM: Putian manure; BJC: Beijing compost; JXC: Jiaxing compost; PTC: Putian compost; BJS: Beijing soil; JXS: Jiaxing soil; PTS: Putian soil.

**Table 2** Tetracyclines in swine manure samples (unit:  $\mu\text{g/kg dw}$ )<sup>a</sup>

Compound	BJM	JXM	PTM
TC	2.2 (0.5)	121.5 (48.9)	1210.0 (910.6)
ETC	2.4 (0.4)	128.4 (61.7)	1261.3 (928.3)
ATC	ND	5.0 (2.4)	69.6 (50.9)
EATC	ND	7.2 (2.3)	37.6 (31.3)
OTC	74.9 (23.1)	2544.2 (518.2)	39.2 (33)
EOTC	6.4 (1.6)	410.1 (301.8)	2.5 (2.9)
$\alpha$ -apo-OTC	ND	67.4 (33.9)	126.8 (204.3)
$\beta$ -apo-OTC	ND	6.5 (3.8)	6.4 (10.4)
CTC	7.9 (1.6)	67.4 (11.8)	8991.8 (6592.2)
ICTC	2.3 (0.3)	6.2 (1.3)	1830.2 (1281.0)
ECTC	15.9 (3.3)	230.4 (36.7)	386.9 (670.1)
ACTC	ND	ND	4.6 (3.3)
EACTC	ND	ND	3.3 (1.3)
MTC	ND	12.0 (5.9)	71.1 (114.2)
DXC	5.1 (0.5)	1350.7 (247.4)	1222.7 (1324.8)
TCs	117.1 (28.4)	4956.9 (1042.1)	15264.0 (7427.0)

<sup>a</sup> The values represent the means  $\pm$  standard.

TC: tetracycline; ETC: 4-epitetracycline; ATC: anhydrotetracycline; EATC: 4-epianhydrotetracycline; OTC: oxytetracycline; EOTC: 4-epioxytetracycline;  $\alpha$ -apo-OTC:  $\alpha$ -apo-oxytetracycline;  $\beta$ -apo-OTC:  $\beta$ -apo-oxytetracycline; CTC: chlortetracycline; ICTC: isochlortetracycline; ECTC: 4-epi-chlortetracycline; ACTC: anhydrochlortetracycline; EACTC: 4-epi-anhydrochlortetracycline; MTC: methacycline; DXC: doxycycline; ND: not detected.

Beijing. Antibiotic residues in manure samples from Ji-axing were detected at the concentration of 4956.9  $\mu\text{g/kg dw}$ . These data can indirectly reflect the regulated use of veterinary antibiotics in Beijing.

Among the different TCs, the OTC concentration contributes more than half of the total concentration for samples from Beijing ( $74.9 \pm 23.1 \mu\text{g/kg dw}$ ) and Ji-axing ( $2544.2 \pm 518.2 \mu\text{g/kg dw}$ ) swine farms, while CTC had the highest percentage for manure samples from Putian ( $8991.8 \pm 6592.2 \mu\text{g/kg dw}$ ). Karci and Balcioglu (2009) detected an OTC concentration of about 500  $\mu\text{g/kg}$  in fresh poultry manure. Even higher concentrations of OTC (70436  $\mu\text{g/kg}$ ) were also reported in the faces of calves treated orally with OTC, which may be attributed to the poor absorption of OTC due to complexation with calcium ions along the gastrointestinal tract of milk-fed calves (De Liguoro et al., 2003). Hamscher et al. (2002) reported that liquid manure contained 100  $\mu\text{g/kg}$  CTC, which was comparable to the samples from Ji-axing. Tylová et al. (2010) detected CTC in liquid hog manure at a concentration of 5880  $\mu\text{g/kg}$ . In China, the detection frequency of OTC

or CTC was generally high. The detected OTC and CTC concentrations have been reported in the range of 0.15–59.06  $\text{mg/kg}$  and 0.16–21.06  $\text{mg/kg}$ , respectively, in pig dung samples from eight provinces of China (Zhao et al., 2010). The average OTC concentration of 2.69  $\text{mg/kg}$  was similar to the determined value in Ji-axing and the average CTC concentration of 1.15  $\text{mg/kg}$  was higher than those in Beijing and Ji-axing, but much lower than that in Putian (Zhao et al., 2010). Furthermore, TC was detected in the selected three swine farms with a similar concentration trend as for CTC, that is, Putian (1210.0  $\mu\text{g/kg dw}$ ) > Ji-axing (121.5  $\mu\text{g/kg dw}$ ) > Beijing (2.2  $\mu\text{g/kg dw}$ ). TC detected in pig manure samples in Austria was in the range of 0.36–23  $\text{mg/kg}$  and was much higher than this study (Martínez-Carballo et al., 2007). The main degradation products of TCs detected in swine manure were their epimers ETC, ECTC and EOTC, which is in agreement with the reported literature that TCs can be excreted in the form of their 4-epimers (Brambilla et al., 2007). Especially for ETC, the concentration was nearly as much as that of TC. Dehydrated products and 4-epianhydrotetracyclines of TC and CTC tended to be lower than their parent TCs. DXC is also one of the most commonly used antibiotics in food-producing animals and it was found in relatively higher concentration in swine manure of this study. The average DXC concentrations were 1350.7 and 1222.7  $\mu\text{g/kg}$  for manure sampled from Ji-axing and Putian, respectively, which were higher than the geometric mean concentration (790  $\mu\text{g/kg}$ ) reported by Zhao et al. (2010). In addition,  $\alpha$ -apo-OTC,  $\beta$ -apo-OTC and MTC were also discovered in Ji-axing and Putian manure samples.

## 2.2 Occurrence of tetracyclines in manure-based compost

Many studies have demonstrated that the concentrations of antibiotics excreted with feces and urine can be significantly decreased during composting (Arikan et al., 2007; Dolliver et al., 2008). In this study, the concentrations of TCs in manure-based compost also declined greatly compared to those in swine manure and individual compounds showed similar concentration trends (Table 3). The average final concentrations for Ji-axing and Putian compost samples were 451.9 and 850.8  $\mu\text{g/kg dw}$ , respectively. However, the decrease was relatively low for the Beijing compost sample with a final concentration of 88.3  $\mu\text{g/kg}$ . Although the detailed composting techniques were not available, it could be inferred that further removal was very difficult when the initial concentration was low. At present, there is no regulated guideline to limit the concentrations of TCs in composts in China. Kwon et al. (2011) used the guideline concentration that appeared in the 'Official Standard of Feeds' under the 'Control of Livestock and Fish Feed Act' in Korea (800  $\mu\text{g/kg}$  for TCs) as a control point to monitor the residues of the target veterinary antibiotics in manure-based compost. According to this guideline concentration, the compost sample from Putian exceeded the value.

TC, OTC, CTC and the associate epimers ETC, EOTC and ECTC were the main detected compounds after

**Table 3** Tetracyclines in manure-based compost samples (unit:  $\mu\text{g/kg dw}$ )\*

Compound	BJC	JXC	PTC
TC	6.4 (0.5)	54.5 (4.0)	51.3 (50.4)
ETC	3.4 (0.4)	29.7 (3.5)	24.6 (20.7)
ATC	ND	ND	ND
EATC	ND	ND	ND
OTC	65.2 (2.9)	70.8 (5.8)	23.2 (8.4)
EOTC	13.2 (2.5)	22.2 (4.2)	9.3 (4.1)
$\alpha$ -apo-OTC	ND	ND	ND
$\beta$ -apo-OTC	ND	3.1 (0.0)	1.7 (1.0)
CTC	ND	73.7 (2.0)	333.8 (341.1)
ICTC	ND	14.5 (2.1)	4.0 (2.3)
ECTC	ND	181.0 (24.4)	324.5 (279.7)
ACTC	ND	ND	ND
EACTC	ND	ND	4.1 (3.4)
MTC	ND	ND	ND
DXC	ND	2.5 (0.2)	74.4 (58.9)
TCs	88.3 (1.7)	451.9 (31.6)	850.8 (746.8)

\* The values represent the means  $\pm$  standard.  
ND: not detected.

composting (Table 3). Anhydrotetracyclines were not detected except that EACTC was found in rather limited concentration in Putian compost. Wu et al. (2011) also discovered none of the 4-epianhydrotetracyclines of the three parent tetracyclines during composting and the slight alkaline condition was thought to be the reason since anhydrotetracyclines could only be formed under strongly acidic conditions. ICTC was also found in compost samples from Jiaying and Putian and a similar result has been reported (Arikan et al., 2009). In general, the relatively high tetracycline residues in Putian compost was most likely related to the initial high concentrations of the antibiotics in raw manures, which implied the potential for TCs to be delivered to the soil environment following application of this compost.

### 2.3 Occurrence of tetracyclines in soil

Consistent with the compost samples, TC, OTC, CTC and their epimers were frequently detected in soil samples (Table 4), indicating their transfer from compost to soil was responsible for their occurrence in the soils (Karci and Balcioglu, 2009). Different from the manure samples, none of the dehydrated compounds were discovered in soil samples. It had been reported that the degradation products ATC, EATC, ACTC and ECTC were more toxic than the parent (Halling-Sørensen et al., 2002), thus, the toxic effect of soil could be reduced considerably when applying composted manure instead of raw manure. Although CTC and its degradation product ECTC were not detected in Beijing compost samples, these chemicals contributed more than half the total concentrations in soil samples, indicating repeated application of compost is likely to pose a probable threat to the environment (Martínez-Carballo et al., 2007). Few field studies on levels of veterinary antibiotics in soil after amending with manure compost have been published. Hamscher et al. (2002) determined the highest mean concentrations of TC in soil fertilized with liquid manure to be up to 198.7  $\mu\text{g/kg}$  in May 2001. Andreu et al. (2009) detected TCs at the concentration of 127.3  $\mu\text{g/kg}$  in soils fertilized with sewage sludge. The

**Table 4** Tetracyclines in soil samples (unit:  $\mu\text{g/kg dw}$ )\*

Compound	BJS	JXS	PTS
TC	ND	5.1 (2.3)	90.0 (14.7)
ETC	ND	3.2 (1.6)	41.4 (14.6)
ATC	ND	ND	ND
EATC	ND	ND	ND
OTC	1.6 (0.8)	4.5 (2.5)	12.3 (1.9)
EOTC	ND	2.0 (1.9)	2.5 (0.7)
$\alpha$ -apo-OTC	ND	ND	ND
$\beta$ -apo-OTC	ND	ND	ND
CTC	1.6 (0.6)	21.2 (5.0)	239.4 (48.1)
ICTC	ND	1.0 (0.5)	35.4 (13.1)
ECTC	1.5 (0.4)	35.3 (16.0)	346.4 (128.1)
ACTC	ND	ND	ND
EACTC	ND	ND	ND
MTC	ND	ND	ND
DXC	ND	8.6 (5.3)	8.6 (0.4)
TCs	4.7 (1.8)	81.0 (34.1)	776.1 (179.1)

\* The values represent the means  $\pm$  standard.  
ND: not detected.

detected maximum concentration of 776.1  $\mu\text{g/kg}$  TCs in soils fertilized with manure compost of this study was higher than the above reported data but much lower than the maximum OTC concentration of 2683  $\mu\text{g/kg}$  detected in winter soil from organic vegetable bases, Tianjin, China (Hu et al., 2010).

The soil trigger value of antibiotics for proceeding to environmental toxicity evaluation was increased from 10 to 100  $\mu\text{g/kg}$  by the Veterinary International Committee on Harmonization (VICH, 2000). Although the total concentrations of TCs decreased sharply after composting, the new trigger value is still exceeded in soil samples from Putian (776.1  $\mu\text{g/kg dw}$ ) after application of the manure-based compost. The accumulation may result from the relatively high antibiotics concentration in the applied compost as well as a rate of application to soils exceeding the degradation rate of tetracyclines. Soil bacteria exposed to these concentrations may experience acute toxic effects and this could affect the composition and function of soil microbial flora. Soils from Jiaying (81.0  $\mu\text{g/kg dw}$ ) had a concentration of the tetracycline class of antibiotics between 10 and 100  $\mu\text{g/kg}$ , and the total concentration in soils from Beijing (4.7  $\mu\text{g/kg dw}$ ) falls below the old trigger value of 10  $\mu\text{g/kg}$ . It has been reported that even very low quantities of antibiotics encouraged the emergence of antibiotic resistant bacteria, not to mention pathogenic bacteria which may also develop resistance to these substances. Therefore, further study is needed to understand the environmental fate of these antibiotics, as well as to evaluate the potential impact of these antibiotics on the soil ecosystem, especially on soil microorganisms.

### 3 Conclusions

The results showed that the studied manure, compost and soil samples were contaminated by TCs and the highest concentration of total TCs was detected in manure samples from Putian. CTC and its degradation products should be regarded critically concerning their potential ecotoxicity. This study revealed significant dilution effects

of antibiotics after manure composting then application in soil, and indicated that use of manure-based compost could decrease the possible risk posed by antibiotic contamination. However, repeated fertilization of soils with manure-based compost may also contribute to the development of antibiotic resistant microbial populations; therefore it is important to monitor the environmental fate of TCs in soil and guidelines should be strictly established and followed for manure-based compost production.

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