Occurrence of 13 veterinary drugs in animal manure-amended soils in Eastern China

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HIGHLIGHTS

- Occurrence of veterinary compound residues were investigated in the study area.
- More than 80% of the sampled soils were contaminated by the selected compounds.
- The animal wastes were one of pollution sources of veterinary drugs in soil.
- The occurrence of selected veterinary drugs in soils was related to animal species.

ARTICLE INFO

Article history:
Received 5 June 2015
Received in revised form 28 October 2015
Accepted 30 October 2015
Available online 22 November 2015

Handling editor: Klaus Kümmerer

Keywords:
Occurrence
Veterinary drug
Manure
Soil
HPLC–MS/MS

ABSTRACT

The occurrence of 13 veterinary drugs were studied in soil fertilized with animal manures in Eastern China. The 69 soil samples were obtained from twenty-three vegetable fields in 2009 and analysed for selected veterinary drugs by HPLC–MS/MS at soil depths of 0–20, 20–40 and 40–60 cm, and two additional samples were re-analysed from an earlier study from November 2011. Results showed that animal wastes, especially those from poultry farms, were one of pollution sources of veterinary drugs in soil. The detection frequency of veterinary drugs in soil was 83%, 91% and 87% in the three soil depths, respectively. The detection rates for the five classes of drugs in soils followed the rank order cyromazine > tetracyclines > sulfonamides > fluoroquinolones > florfenicol. Veterinary drugs were detected in soil layers at 20–40 and 40–60 cm depth to a greater extent than at 0–20 cm depth. The results of the same point in years 2009 and 2011 indicated that veterinary drugs accumulate easily and persist in the deeper soil. In addition, residue levels of veterinary drugs in soil were related to the animal species the manure was derived from. Overall, the predominance of tetracyclines in sampled soils underscored the need to regulate their veterinary use in order to improve the management and treatment of associated releases.

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1. Introduction

Veterinary antimicrobial drugs are biologically active substances designed to kill microbes or inhibit their growth. In modern animal agriculture, most veterinary drugs fed to animals are poorly absorbed in the animal gut and up to 90% of them may be excreted either as a parent compound or in a partially metabolized form (Tolls, 2011). Veterinary drugs have the potential to enter the environment through animal manure fertilizers and can persist in soils for a long time (Förster et al., 2009). An increasing number of reports show a rise in the occurrence and distribution of veterinary drugs in excrement and environment in various countries throughout the world (Manzetti and Ghisi, 2014). Moreover, veterinary drugs may be taken up by crop plants from manure-amended soils and can be transported to ditches, streams and rivers via runoff and drain flow to groundwater via leaching (Boonsaner and Hawker, 2015; Blackwell et al., 2009).

With the increase in use of veterinary antibiotic drugs in animal production, there is a growing concern that excreted drugs have potentials to encourage the selection of antimicrobial resistance and spread in the environment (Heuer et al., 2011). The applications of veterinary antibacterials as growth promoters in animal feeds are now strictly regulated in various countries and even totally prohibited in the European Union since 2006 and in the United States (Alban et al., 2008; Food and Drug Administration, 2003). But this practice still continues in other countries including...
China which is one of the world’s largest producers and exporters of animal products. Large quantities of manure containing various antibacterials are produced and stored in manure pits for subsequent application or applied immediately to land (Boxall, 2008). However, only a few studies on occurrence and fate of veterinary drugs in manure-amended soil have been done in China (Hu et al., 2010; Ostermann et al., 2013; Li et al., 2014). Therefore, limited information is available on the presence and distribution of veterinary drugs in the various layers of manure-amended soil.

The present study was designed to investigate the occurrence of tetracyclines (TCs), sulfonamides (SAs), fluoroquinolones (FQs), cyromazine (CY) and florfenicol (FF) at three soil depths of 0–20, 20–40 and 40–60 cm collected from vegetable fields that used animal manure as fertilizer. To our knowledge, veterinary drugs as a source of environmental pollution have been largely ignored in China. This work embodies the first widespread investigation on the occurrence of important classes of veterinary compounds in the soil, especially in deeper soil in Eastern China. The results could provide useful information for assessing the impacts or potential risks of veterinary drugs to ecosystems and for proper handling of antibiotic-containing manure.

2. Materials and methods

2.1. Chemicals

Sulfadiazine (SDZ), sulfamethoxazole (SMX), sulfamethazine (SMZ), sulfadinoxine (SQX), sulfadoxine (SDX), chlorotetracycline (CTC), oxytetracycline (OTC), tetracycline (TC), doxycycline (DOX), florfenicol (FF), enrofloxacin (ERFX), ciprofloxacin (CPFX) and cyromazine (CY) were obtained from Dr. Ehrenstorfer Gmbh (Augsburg, Germany). Formic acid, methanol and acetoneitrile (HPLC/MS-grade) were purchased from ROE Scientific INC (Newark, USA). Ultra-pure water was prepared with a Milli-Q water purification system (Millipore, USA). Unless otherwise indicated, chemicals used were purer than the analytical grade. All the drugs were dissolved to create the 100 mg L$^{-1}$ stock solution in methanol with the exception for fluoroquinolone drugs, which were prepared in methanol containing 0.5% 1 M NaOH, from which a 7-point calibration curve was created. The stock solutions were stored at $−20^\circ$C and were stable for at least two months except for TCs and FQs. The working solutions were prepared freshly on the day of use.

2.2. Study site and sample collection

The study domain was located in Jiangsu Province, which is one of the most developed economic areas in China, and large-scale livestock and poultry production was initiated in this area earlier than other regions of the country. The study region covers an area of about 102 600 km$^2$, and the plain area is 70 600 km$^2$. Situated in a transition belt from a subtropical to temperate zone, it has a typical monsoon climate with moderate amounts of rainfall. The average organic matter content, pH and cation exchange capacity of soil in this region were 21 g kg$^{-1}$, 7.2 and 13 cmol kg$^{-1}$, with coefficients of variation of 35%, 17% and 41%, respectively.

The soils were collected from twenty-three sites (designated as S1 to S23 in Fig. 1) located in vegetable fields. All fields had a history of manure application from large-scale livestock and poultry operations. Soil samples were taken from 5 locations at each site as the S type for the different depths ($0$–20, 20–40 and 40–60 cm) and the soil samples from each depth were mixed. The samples were transported under cooled conditions to the laboratory and lyophilized. The $≤2$ mm fraction was separated and stored in the dark at $−20^\circ$C before further treatment and analysis. The 69 soils sampled in April 2009 and two additional samples (S5 and S13) re-analysed from an earlier study in November 2011, were extracted and the extracts analysed for selected veterinary drugs by high performance liquid chromatography/tandem mass spectrometry (HPLC–MS/MS).

2.3. Extraction

Extraction procedures for target compounds in soil were developed based on methods reported by Martínez-Carballo et al. (2007). The 3.0 g soil sample was added into 50 mL centrifuge tube with 9 mL methanol and then 1 mL of 0.1 M Na$_2$EDTA-McIlvaine solution (pH 6) was added to prevent complexation between veterinary drugs and multivalent cations. The solution was homogenized for 30 s by vortex mixing and then ultrasonically extracted for 20 min in a bath sonicator. The supernatant was moved to a clean tube after centrifugation at 5000 r min$^{-1}$ (4 $^\circ$C) for 10 min. This procedure was performed in triplicate and the supernatants were pooled.

The supernatant was applied to a polymeric Oasis HLB cartridge (6 mL, 500 mg), which had been preconditioned with 5 mL of methanol and 5 mL 0.1 M Na$_2$EDTA-McIlvaine solution (pH 4). After the supernatant was loaded into the cartridge, the cartridge was rinsed with 10 mL of ultrapure water, and then eluted with 6 mL 0.01 M oxalic acid in methanol. The eluate was evaporated to near dryness under a gentle stream of nitrogen and the residue was dissolved with the HPLC mobile phase. The resulting solution was filtered through a 0.22 μm disposable nylon syringe filter and 10 μL was injected into the HPLC–MS/MS system.

2.4. Liquid chromatography/tandem mass spectrometry and quantification

Separation of veterinary drugs was performed by HPLC using an Agilent 1200 system with an Agilent Zorbax RX-C$_8$ column (2.1 × 150 mm, 5 μm). The mobile phase consisted of water (Solvent A) and acetonitrile (Solvent B) both acidified with 0.1% formic acid. The gradient was held at 10% B for 15 min, then run from 10% B to 30% B in 10 min, kept at 30% B for 8 min, then run from 30% B to 90% B in 1 min and kept 90% B to 40 min. The quantitation of target compounds was determined by Mass Spectroscopy using an Agilent 6410 triple quadrupole mass spectrometer with an electrospray ionization (ESI) source. Standard compounds (1 mg L$^{-1}$) were infused through an integrated syringe pump to tune the mass spectrometer and to optimize capillary temperature, nebulizer pressure and drying gas flow rates. The source polarity was set in the positive ionization mode for CY, TCs, SAs and FQs, and in negative ionization mode for FF, respectively. The optimized conditions were as follows: capillary temperature of 350 $^\circ$C, drying gas flow of 10 L min$^{-1}$, nebulizer pressure of 40 psi (2.76 bar), capillary voltage of 4.0 kV. Nitrogen (≥99.995%) was used as the cone and collision gas. More detailed MS–MS parameters have been reported in previously published studies (Wei et al., 2011, 2012).

The recovery studies were carried out with control soils spiked at the 5, 25, and 100 μg kg$^{-1}$ levels. The extraction procedure was performed after 30 min equilibration. The control soil was prepared from 13 drug-free soil samples taken at depths of 0–20 cm, 20–40 cm, and 40–60 cm in the vicinity of the soil-monitoring site under investigation. The recovery rate was calculated as an average of eight experiments at each concentration. The quantification limit of the method (MQL) was defined as the lowest concentration of analytes that can be determined with acceptable precision and accuracy from the residue-free samples spiked at different levels (Martínez-Carballo et al., 2007; Boon et al., 2006). Table 1 summarized the results of MQL recovery and relative standard deviation of the soils spiked with 13 veterinary drugs.
Matrix effects of the analytical procedure were evaluated with spiked blank soil samples. The analytical results were compared to direct injection of standard mixture at the same concentration. The results indicated that matrix effects existed in soils in this study. But this analytical method was accepted because the recoveries of spiked blank soils samples were in the 50.3–80.7% range and RSD was lower than 15%.

3. Results and discussion

3.1. Occurrence of selected veterinary drugs in three soil layers

This study determined the occurrence of veterinary drugs including five SAs, four TCs, two FQs, one CY and FF in soil from vegetable fields at 0–20, 20–40 and 40–60 cm deep from Jiangsu

<table>
<thead>
<tr>
<th>Drug</th>
<th>0–20 cm</th>
<th>20–40 cm</th>
<th>40–60 cm</th>
<th>Average recovery (%)</th>
<th>MQL</th>
</tr>
</thead>
<tbody>
<tr>
<td>CY</td>
<td>74</td>
<td>7.6</td>
<td>52.8</td>
<td>74</td>
<td>3.7</td>
</tr>
<tr>
<td>SAs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SDZ</td>
<td>4</td>
<td>ND</td>
<td>20.9</td>
<td>13</td>
<td>5.3</td>
</tr>
<tr>
<td>SMZ</td>
<td>22</td>
<td>15.3</td>
<td>30</td>
<td>15.6</td>
<td>1316</td>
</tr>
<tr>
<td>SMX</td>
<td>13</td>
<td>5.9</td>
<td>26</td>
<td>1.6</td>
<td>1784</td>
</tr>
<tr>
<td>SDX</td>
<td>4</td>
<td>ND</td>
<td>33.2</td>
<td>22</td>
<td>1.5</td>
</tr>
<tr>
<td>SQX</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>TCs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OTC</td>
<td>52</td>
<td>34.4</td>
<td>3511</td>
<td>39</td>
<td>41.1</td>
</tr>
<tr>
<td>TC</td>
<td>26</td>
<td>26.0</td>
<td>763</td>
<td>17</td>
<td>20.2</td>
</tr>
<tr>
<td>CTC</td>
<td>39</td>
<td>256</td>
<td>4723</td>
<td>22</td>
<td>86.3</td>
</tr>
<tr>
<td>DOX</td>
<td>9</td>
<td>7.0</td>
<td>10.8</td>
<td>13</td>
<td>13.8</td>
</tr>
<tr>
<td>FQs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CPFX</td>
<td>13</td>
<td>9.0</td>
<td>9.4</td>
<td>39</td>
<td>9.9</td>
</tr>
<tr>
<td>ERFX</td>
<td>4</td>
<td>ND</td>
<td>3.0</td>
<td>35</td>
<td>3.5</td>
</tr>
<tr>
<td>FF</td>
<td>9</td>
<td>4.0</td>
<td>4.1</td>
<td>9</td>
<td>4.0</td>
</tr>
</tbody>
</table>

- Number of samples analysed.
- Frequency, %.
- Median.
- Maximum.
- Not detected.
- Method quantitation limit (μg kg⁻¹).
Province of East China. Among 69 soil samples, the positive detection frequency for antimicrobials in soil was 83%, 91% and 87% at 0–20, 20–40 and 40–60 cm depths, respectively. The overall detection rates of CY were 74%, 74% and 43% at different soil depths, respectively; SAs were 30%, 35% and 35%, respectively; TCs were 61%, 52% and 52%, respectively; FQs were 13%, 39% and 30%, respectively; and FF were 9%, 9% and 26%, respectively. On the whole, the detection rates for the five classes of drug in soils followed the rank order CY > TCs > SAs > FQs > FF.

The detection frequency and concentrations of selected veterinary drugs in sampled soils is summarized in Table 1. Two drugs were found to have detection frequencies above 50% at a depth of 0–20 cm, with CY being the most frequently detected (74%) followed by OTC (52%). Other drugs with moderate detection frequencies (20–50%) were CTC (39%), TC (26%) and SMZ (22%). The maximum concentrations in the 0–20 cm collected samples were 52.8 μg g⁻¹ for CY, 3511 μg g⁻¹ for OTC, 4723 μg g⁻¹ for CTC, 763 μg g⁻¹ for TC, and 100 μg g⁻¹ for SMZ.

The detection frequency of CY was 74% at a depth of 20–40 cm, followed by OTC 39%, CPPX 35%, ERFX 35%, SMZ 30%, SMX 26%, SDX 22% and CTC 22%. The maximum concentrations for these veterinary drugs were 40.1, 1549, 7220, 3059, 1316, 1784, 924 and 30,779 μg g⁻¹, respectively.

The detection frequency of eight drugs ranged from approximately 20%–50% in soils of 40–60 cm depth, CY 43%, SMZ 35%, SMX 22%, SDX 22%, OTC 39%, CTC 22%, CPFX 30% and FF 26%. The corresponding maximum concentrations for the drugs were 36.9, 1688, 1692, 1163, 3676, 86,567, 5305 and 11.4 μg g⁻¹, respectively.

Previous studies indicated that residues of veterinary drugs in animal excrement were common in China. CPFX, ERFX and TC were found in swine and cow manure at levels up to several tens mg kg⁻¹, whereas ERFX in poultry manure and OTC in pig manure were detected at levels up to 1420 and 354 mg kg⁻¹, respectively (Zhao et al., 2010; Chen et al., 2012). Therefore, when the manure was used to fertilize the land, the soil would likely be contaminated with these compounds. Researchers from USA, China, Australia and Turkey have detected residues of TCs, SAs and FQs in the soil that had been fertilized with animal manure (Ostermann et al., 2013; Martínez-Carballo et al., 2007; Aga et al., 2005; Karci and Balcioglu, 2009). In the present study, the concentrations of veterinary drugs in the ppb to ppm ranges in soil of 0–20, 20–40 and 40–60 cm depths were basically consistent with their detection frequency and increased as the soil depth increased. For example, the concentration of ERFX in sampled soil at depth of 20–40 cm was 1000 times that at depth of 0–20 cm. This result indicated that those veterinary drugs were frequently used to prevent and treat animal diseases or promote the growth of animal as feedstuff additives. It also indicates that the application of contaminated animal manure to fields and its subsequent ploughing can cause the accumulation and persistence of veterinary drugs in soils used for crop production.

3.1.1. Cyromazine (CY)

CY has been approved in 2002 by the Ministry of Agriculture of China as a veterinary drug in order to prevent flies from hatching in manure. The most CY taken orally by animals is excreted through feces as the original compound (75–86%) (Keiding, 1999). It has a moderate to high mobility to leach through the soil profile and be transported to deeper soil or contaminate groundwater (Wang et al., 2014). The atmosphere, water and soil were detected in different concentrations of CY (Armenta et al., 2004). The results shown in Table 1 indicated that the widespread use of CY in food-producing animals raises the possibility of residues remaining in the environment along with farmland-application of animal manure. The distribution of concentration for CY in soil layer was as follows: 0–20 cm > 20–40 cm > 40–60 cm.

Earlier studies showed that CY was used to control Diptera larvae in chicken manure by administering the drug in poultry feed or by treating the larvae breeding sites (Liu et al., 2010). Table 2 showed that CY had higher detection frequency and levels in soils applied with poultry manure than that in soils applied with swine and cow manure.

3.1.2. Sulfonamides (SAs)

SMZ showed higher detection frequency and residue levels in the three soil layers than other SA drugs (Table 1). The next most frequently detected and abundant SA was SMX. SMZ and SMX are sulfonamides widely used to prevent and treat veterinary infections or as growth promoters in livestock farming (Kim et al., 2011). They were frequently detected in soils. Residue levels of SDZ, SMZ and SDX in the 20–40 and 40–60 cm soil layers were much higher than those in 0–20 cm soil layer. Moreover, the residual concentrations of SMZ, SMX and SDX in soil exceeded the minimum inhibitory concentrations of SAs for Escherichia coli (Sukul and Spiteller, 2006). SAs are one of the most frequently used antibiotics in modern animal production and up to 90% are excreted from the organisms (Kwon et al., 2011). They are directly added to the soil environment through amending manure to agricultural fields or ploughing practices. In fact, SAs are frequently detected in the environment and have been found in groundwater samples in many places, including Korea, Germany, China, Spain, Taiwan and USA (Kim et al., 2011).

3.1.3. Tetracyclines (TCs)

The OTC, TC and CTC showed higher occurrence than DOX in 0–20, 20–40 and 40–60 cm soil layers in Table 1. One possible explanation for this result is attributed to the relatively higher cost of DOX than other TCs in animal feeding. Table 2 indicated that TCs were one of the dominant antibiotics used in large-scale animal feeding operations in Jiangsu, which were widely used in poultry and swine production, preferred to use DOX in cow production. Literature shows that TC drugs were most frequently used drugs in animal production in China (Jia et al., 2008) and as much as 50–80% of the TCs administered to farm animals remains in their active form in feces and urine (Sarmah et al., 2006). With soil tillage, TC drugs in surface soil are ploughed into the deeper soil layers, which may be the main way of TCs down through the soil since they are believed to bind strongly to the soil matrix (Wan et al., 2010; Schmitt and Schneider, 2000). TC drugs may also be carried into the sub-surface soils via runoff and leaching by rain and irrigation (Kwon et al., 2011). The results of the same point in years 2009 and 2011 showed that soil tillage, weak photodegradation and biodegradation caused TC drugs to persist in the 20–40 and 40–60 cm soil layers (Table 3).

3.1.4. Fluoroquinolones (FQs)

ERFX and CPFX had a higher detection frequency and maximum concentration in 20–40 and 40–60 cm soil layer than that in 0–20 cm soil layer in Table 1. Further analysis showed that they had relatively higher contaminated levels in samples from poultry manure amended soils than those from cow and swine manure amended soils in Table 2. FQs are commonly used to control and prevent respiratory diseases as a feed additive in poultry industry (Dheilly et al., 2011). These molecules undergo only a partial metabolism in the body and they are largely excreted in the active form (Sturini et al., 2012). Concentrations as high as 45.6 and 1420 mg kg⁻¹ of CPFX and ERFX, respectively, were found in
Table 2
Effect of the different animal manures on detection frequency and concentrations ($\mu$g kg$^{-1}$) of veterinary drugs at various soil depths.

<table>
<thead>
<tr>
<th>Drug</th>
<th>Soil applied with manure (n = 27)</th>
<th>0–20 cm</th>
<th>20–40 cm</th>
<th>40–60 cm</th>
<th>0–20 cm</th>
<th>20–40 cm</th>
<th>40–60 cm</th>
<th>0–20 cm</th>
<th>20–40 cm</th>
<th>40–60 cm</th>
<th>0–20 cm</th>
<th>20–40 cm</th>
<th>40–60 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>CY</td>
<td>100</td>
<td>3.8</td>
<td>89</td>
<td>40.1</td>
<td>67</td>
<td>3.3</td>
<td>50</td>
<td>9.0</td>
<td>6.6</td>
<td>3.3</td>
<td>50</td>
<td>9.0</td>
<td>3.3</td>
</tr>
<tr>
<td>SAs</td>
<td>22</td>
<td>100</td>
<td>100</td>
<td>13.7</td>
<td>1386</td>
<td>12</td>
<td>17</td>
<td>26</td>
<td>461</td>
<td>22</td>
<td>17</td>
<td>26</td>
<td>461</td>
</tr>
<tr>
<td>TCs</td>
<td>22</td>
<td>15.3</td>
<td>34</td>
<td>704</td>
<td>704</td>
<td>10.3</td>
<td>34</td>
<td>704</td>
<td>704</td>
<td>10.3</td>
<td>34</td>
<td>704</td>
<td>704</td>
</tr>
<tr>
<td>FQs</td>
<td>33</td>
<td>2.9</td>
<td>6</td>
<td>363</td>
<td>363</td>
<td>2.9</td>
<td>6</td>
<td>363</td>
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</tr>
</tbody>
</table>

Table 3
Concentration of selected veterinary drugs in S5 and S13 sites in years 2009 and 2011 ($\mu$g kg$^{-1}$).

<table>
<thead>
<tr>
<th>Site</th>
<th>Substance</th>
<th>20–40 cm</th>
<th>40–60 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2009</td>
<td>2011</td>
<td>2009</td>
</tr>
<tr>
<td></td>
<td>2009</td>
<td>2011</td>
<td>2009</td>
</tr>
<tr>
<td>S5</td>
<td>OTC</td>
<td>1549</td>
<td>904</td>
</tr>
<tr>
<td></td>
<td>TC</td>
<td>4450</td>
<td>4813</td>
</tr>
<tr>
<td></td>
<td>CTC</td>
<td>30,779</td>
<td>21,950</td>
</tr>
<tr>
<td></td>
<td>2009</td>
<td>2011</td>
<td>2009</td>
</tr>
<tr>
<td></td>
<td>2009</td>
<td>2011</td>
<td>2009</td>
</tr>
<tr>
<td>S13</td>
<td>OTC</td>
<td>3676</td>
<td>2986</td>
</tr>
<tr>
<td></td>
<td>TC</td>
<td>21,950</td>
<td>86,567</td>
</tr>
<tr>
<td></td>
<td>CTC</td>
<td>86,567</td>
<td>58,046</td>
</tr>
</tbody>
</table>

chicken manures from China (Zhao et al., 2010). FQs may enter the soil via good agricultural practice and leaching and can accumulate due to their adsorption to soil matrix and their low degradability in soil (Pereira Leal et al., 2012). In the present study, ERFX was present at much smaller quantities than CPFX in different soil layers. This phenomenon could be due to the metabolic conversion of ERFX into CPFX that occurs in many species (Lewis et al., 2011). These results are in agreement with those of Li et al. (2014), who also detected ERFX and CPFX in a soil-vegetable system in an intensive vegetable cultivation area in Northern China. Residual levels of FQs have also been reported in manured soils in many countries, including Brazil, Turkey, China, Austria and France, at concentrations of up to 518 $\mu$g kg$^{-1}$ for ERFX and 651.6 $\mu$g kg$^{-1}$ for CPFX (Li et al., 2014; Martínez-Carballo et al., 2007; Karci and Balcioglu, 2009; Dheilly et al., 2011).

3.1.5. Florfenicol (FF)
FF has been approved for use in veterinary medicine in the European Union, USA, Canada, Japan, Korea, China and other countries. It is regarded as an important drug that is commonly administered as premix at a level of 4% or higher to treat respiratory disease in animal farms (Hayes et al., 2009). In this study, the concentration and frequency of FF detected were not high than other target compounds except ERFX at three depths of 0–20, 20–40 and 40–60 cm, suggesting that FF was not commonly used in animal farms. Nowadays, there are few cases concerning the presence of FF residues in soils or their migration from manure to soil. This may be due to differences in veterinary practice, where FF was mainly used in aquaculture in many overseas countries (Pouliquen et al., 2009; Miranda and Rojas, 2007).

3.2. Effect of different sources of animal manure on occurrence of veterinary drugs in soils

The occurrence of 13 veterinary drugs in soil treated with different animal manures is summarized in Table 2. The result indicated that the frequency of detection of drugs in soil fertilized with animal manure from different sources followed the rank order: poultry-manured soil > swine-manured soil > cow-manured soil. TCs are widely used in the poultry and swine industry for growth promotion and disease treatment or prevention (Kemper, 2008). Because CY is mainly used to prevent flies from hatching in manure, it was detected at a relatively high frequency in soils fertilized with poultry, cow and swine manure (Liu et al., 2010).

The occurrence of veterinary drugs in the sampled soil also illustrates that these compounds have been used widely and for long durations in this region for animal production. CY, SAs, TCs and FQs were frequently detected at high levels in poultry-manured soil, suggesting they were widely used and have high consumption rates in poultry farms. The intensive production of poultry in China increases the susceptibility to disease outbreaks and necessitates the use of medicated diets.

The frequency of veterinary drugs detected in soils fertilized with cow manure had the following rank order with respect to soil depth: 40–60 cm > 20–40 cm > 0–20 cm. The residue levels of seven drugs, including SDZ, SMZ, SMX, SDX, OTC, TC and
CTC, were relatively high in soil layer at 40–60 cm. For example, TC and CTC were observed with maximum concentrations of 10.2 and 86.5 mg kg⁻¹, respectively. Following the Chinese milk incident in 2008 in which infant formula was contaminated with melamine (Ji et al., 2014), the Chinese government administered more rigorous supervision of veterinary drugs used in milk production. Cow farmers in China prefer to use herbs for the treatment of cow diseases such as mastitis, thus reducing the amount of veterinary drugs consumed on cow farms compared to that in poultry and swine farms.

CY, SMZ and TCs were found in soils fertilized with swine manure at 0–20, 20–40 and 40–60 cm deep. Eleven veterinary drugs were detected at depth of 20–40 cm, suggesting that these compounds were commonly used in swine farms.

4. Conclusions

This study provided an overview on the occurrence of 13 veterinary drugs in animal manure-amended soils at depths of 0–20, 20–40 and 40–60 cm in Jiangsu Province in Eastern China. The results showed that more than 80% of the sampled soils were contaminated by the selected compounds at three soil depths. As was expected, animal waste especially those from poultry production can act as an important non-point source of veterinary drug residues in soils. The detection rates of these compounds in soils followed the rank order: CY > TCs > SAs > FQs > FF. The occurrence of selected veterinary drugs in soils was related to animal species. The classes, amount and frequency of veterinary drugs were considerable in soils applied with poultry and swine manure. Veterinary drugs can be taken up by crop plants from manure-amended soils. There is an increasing concern regarding the environmental pollution and food safety implications caused by veterinary drug contamination of soils. Further research is needed to evaluate the impact of these compounds on the environment, environmental biota, and public health.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Grants No 21307044 and No 31302009) and the Special Public Project of Ministry of Environmental Protection of China (200809092A).

References


