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Investigation of residual fluoroquinolones in a soil–vegetable system in an intensive vegetable cultivation area in Northern China

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HIGHLIGHTS

- The spatial pattern of FQs in the soil showed obvious heterogeneity.
- The accumulation ability of FQs was different among vegetable species.
- The transfer ability of NOR in soil–vegetables is greater than that of CIP and ENR.

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ABSTRACT

One of the largest vegetable cultivation field sites in Northeast China was selected to investigate the occurrence and distribution pattern of fluoroquinolones (FQs) in the soil–vegetable system. A total of 100 surface soil samples and 68 vegetable samples were collected from this study area. The antibiotic concentration was analyzed using high-performance liquid chromatography tandem mass spectrometry. Results indicated the presence of FQs in all soil samples. Ciprofloxacin (CIP) had the highest mean concentration, at 104.4 $\mu g \cdot kg^{-1}$ in the soil, a level that represents a relatively high risk to the environment and to human health. However, in the vegetable samples, norfloxacin (NOR) was significantly higher than CIP and enrofloxacin (ENR), ranging from 18.2 to 658.3 $\mu g \cdot kg^{-1}$. The transfer ability of NOR in soil–vegetables is greater than that of CIP and ENR. Moreover, we found that the solanaceous fruits had a higher antibiotic accumulation ability than the leafy vegetables. Taken together, these data indicate that greater attention should be paid to the region in which vegetables with higher accumulation ability are grown.

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1. Introduction

Antibiotics are widely used to treat animal diseases. However, antibiotics that are not fully absorbed are excreted in the feces, and various antibiotics have been detected in the feces of livestock and poultry at levels as high as hundreds of milligrams per kilogram of feces (Karci and Balcioglu, 2009; Martinez-Carballo et al., 2007; Pan et al., 2011). Since feces are rich in various plant nutrients (e.g., nitrogen, phosphorous, and potassium), livestock manure has traditionally been an important ingredient in organic and sustainable farming systems (Kumar et al., 2005) and is applied to crops in its native form or as compost. In the areas of intensive vegetable farming, the nutrient requirement for vegetable growth is relatively high. Because the use of chemical fertilizers is restricted for organic vegetables, to meet this requirement livestock and poultry feces are often applied to the soil to aid vegetable growth. In such cases, a small amount of the antibiotics in the feces may be rinsed off into the surface water or may leach into the groundwater, but most of the antibiotics remain in the soil (Giger et al., 2003; Lee et al., 2007; Wei et al., 2011) where they can be taken up by plants (Dolliver et al., 2007; Migliore et al., 2003). There is evidence of ecotoxic effects of antibiotics on plants (Jin et al., 2009) and soil microorganisms (Schmitt et al., 2005); however, the health implications of antibiotic residues in plant-based products are largely unknown, although it is anticipated that the antibiotic residues may have adverse effects on human health (Chefetz et al., 2008; Martinez, 2008; Xiao et al., 2008).

China is the largest producer and consumer of antibiotics in the world; the estimated annual antibiotics production was about 210 million kg, and 46.1% of these were used in livestock industries (Zhu et al., 2013). However, veterinary antibiotics are poorly absorbed by the animal and hence are excreted. As shown in a relative study, fluoroquinolones (FQs) are among the most frequently detected antibiotics in the feces of farm livestock and poultry in China and the concentration of FQ

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residue is commonly very high. The maximum manure concentration of norfloxacin (NOR), ciprofloxacin (CIP), and enrofloxacin (ENR) can be up to 225.45 $mg \cdot kg^{-1}$, 45.59 $mg \cdot kg^{-1}$, and 1420.76 $mg \cdot kg^{-1}$, respectively, while the geometric mean concentrations are 3.78, 4.65, and 4.68 $mg \cdot kg^{-1}$ (Zhao et al., 2010). The sorption of FQs to the poultry litters was lower than the soil (Leal et al., 2012). Therefore, when livestock and poultry feces are added to the soil as fertilizers, FQs are sorped to the soil particles. The sorption affinity of FQs may result in poor mobility; meanwhile, the degradation rate of FQs is also decelerated, resulting in an accumulation of FQs in the soil over time (Golet et al., 2003; Tolls, 2001; Uslu et al., 2008). Continuous application of livestock and poultry feces and intensive cultivation (i.e., several cultivations per year) in specific areas can result in high residual antibiotic levels.

At present, there are many reports concerning the occurrence of antibiotics in aquatic environments (Hirsch et al., 1999; Luo et al., 2011; Wei et al., 2011). However, relatively few studies focus on the antibiotic residues in the soil of areas of intensive vegetable cultivation (Hu et al., 2010; Li et al., 2011). At present, most research concerning the transformation of antibiotics in a soil–vegetable system are completed in the laboratory (Liu et al., 2009; Migliore et al., 2000, 2003); however, since experimental conditions differ during actual greenhouse cultivation, laboratory research results should be verified in situ. Therefore, the objectives of our study are 1) to investigate the residue levels and spatial pattern of FQ distribution in soil and vegetables in a large number of samples from Shouguang City, the largest vegetable cultivation base in Northern China; and 2) to study the antibiotic accumulation ability in different types of vegetables grown in the study region.

2. Material and methods

2.1. Study area and sampling

The study domain is an important vegetable-growing region located in the north-central part of the Shandong Province of China. The study region covers an area of about 160 km^2. The climate consists of a warm, temperate, continental monsoon climate with seasonal changes (e.g., in summer, hot and rainy; in winter, cold and dry). The annual average temperature is 12.7 °C; the hottest and coldest months are June and January, with monthly average temperature 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.

The vegetables are grown in 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 as 2–3 crops per year, and are fertilized in autumn or winter, 1–2 times per year. Animal manure (chicken manure, cow dung, etc.) 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 application quantity ranged from 1.3 to 17.1 $kg \cdot m^{-2}$ annually.

For the present study, based on the systematic sampling principle, 100 vegetable greenhouses were selected from the study area. The average distance between vegetable greenhouses was approximately 1 km. One surface soil sample was collected from each vegetable greenhouse, totaling 100 samples (Fig. 1). Using a small shovel, soil samples were collected from 0 to 15 cm below the soil surface during November 2010. Five sampling sites were distributed along an S-shaped path within each greenhouse and were then fully mixed to form a single sample. At the same time, the edible parts of each vegetable were sampled according to the soil sample sites in each greenhouse. We also took five vegetable samples that were finally pooled into one composite sample. The total number of vegetable samples is 68 because some of the greenhouses were not growing any edible vegetables. Among the samples collected, the leafy vegetables and solanaceous fruits were most frequent. The samples were immediately transported to a laboratory for analysis under cooled conditions.

2.2. Reagents and analysis

Ciprofloxacin (CIP), enrofloxacin (ENR), and norfloxacin (NOR) were purchased from Sigma (St. Louis, MO, USA) and their purities are all above 98.0%. Acetonitrile and methanol (HPLC grade) were purchased from Fisher (New Jersey, USA). Water was purified using a Milli-Q system (Millipore, Bedford, MA, USA). Oasis HLB (200 mg, 6 mL) cartridges for hydrophilic–lipophilic balances and SAX cartridges (200 mg, 3 mL) were purchased from the Waters Corporation (Milford, MA, USA) and Bonna-Agela Technologies (Tianjin, China). All other reagents were of analytical reagent grade. Stock solutions of the standards were prepared using methanol (100 $\mu g \cdot mL$) and were stored at −20 °C for approximately 1 week. The phosphate buffer was compounded with 1.35 mL of H_3PO_4 and 31.2 g of $NaH_2PO_4 \cdot 2H_2O$ within 1 L of water.

Lyophilized soil (2.0 g) was extracted in 10 mL of phosphate buffer with acetonitrile (1:1 v:v) and sonicated for 15 min, and then were centrifuged at 3000 ×*g* in air-cooled conditions. The extraction procedure was performed 3 times with fresh aliquots of solvent each time, and finally, the supernatants were combined (approximately 30 mL). The Oasis HLB and SAX cartridges were sequentially pre-conditioned with 6.0 mL of methanol and 6.0 mL of Milli-Q water. The mixture containing extraction solution with <5% organic reagent (water dilution was used to reduce the organic solvent concentration) was loaded onto the cartridge at a flow rate of approximately 2.0 $mL \cdot min^{-1}$. The cartridge was then rinsed with 6 mL of Milli-Q water and lyophilized for 40 min. Elution of the antibiotic compounds from the cartridges was performed with 6.0 mL of methanol. Methanol eluate was evaporated to near dryness under a gentle stream of nitrogen and subsequently redissolved with 1.0 mL of methanol.

Lyophilized vegetables (1.0 g) were homogenized and extracted in 10 mL of acetonitrile and hydrochloric acid (125:1, v:v) via ultrasonication for 15 min, and then were centrifuged at 4000 ×*g* in air-cooled conditions for 10 min. After that, the supernatant was poured into a brown bottle. The above extract process was repeated three times with fresh solvent (acid acetonitrile). All the supernatants were mixed in the brown bottle and were liquid–liquid extracted with 20 mL of hexane to eliminate the lipid materials. The extraction process using HLB cartridges was same to that of soil. Moreover, methanol eluate was evaporated to near dryness under a gentle stream of nitrogen and redissolved with 1.0 mL of methanol.

The concentration of FQs (CIP, ENR, and NOR) in soil and vegetable was analyzed using high-performance liquid chromatography tandem mass spectrometry (HPLC–MS/MS) equipped with an electrospray ionization (ESI) source (operated in the positive ionization (PI) mode) and a XDB-C18 column (4.6 × 50 mm, 1.8 μm). Ten microliters of the extract was injected into the chromatographic system. The mobile phase consisted of 0.1% formic acid (A) and acetonitrile (B). The mobile phase gradient was ramped at a flow rate of 0.4 $mL \cdot min^{-1}$ from 10% B to 40% in 6.0 min and 40% to 95% in 2.0 min, kept for 2.0 min, then ramped to 10% in 5.0 min. The column temperature was set to 20 °C. The nebulizer pressure was set to 30 psi and the drying gas was nitrogen. The flow rate and temperature of drying gas were 10 $L \cdot min^{-1}$ and 350 °C, respectively. The capillary voltages were 3000 V. Sample acquisition was performed in the multiple reaction monitoring (MRM) mode. The optimal conditions for analyte monitoring are summarized in Table S1. For accurate results, 10 μL of 10 $ng \cdot \mu L^{-1}$ norfloxacin-d3 (internal standards, ISs) was added to the soil prior to extraction. The detection limits of the 3 antibiotics were all <0.1 $\mu g \cdot kg^{-1}$ and the relative standard deviation (RSD) was in the range of 2.5–5.0%. The absolute recoveries of CFX, EFX, and NFX were about 55–65% in soil samples and about 78–105% in vegetable samples.

2.3. Data analysis

Descriptive statistical analysis was performed to explore the concentration of FQ in soil and vegetables. A nonparametric Kolmogorov–

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