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Distribution and risk assessment of quinolone antibiotics in the soils from organic vegetable farms of a subtropical city, Southern China

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HIGHLIGHTS

- Quinolones in soil of subtropical organic vegetable farms were frequently detected with low concentrations.
- Concentrations of quinolones in open-field soil were higher than in greenhouse.
- Quinolones in soil of the studied farms posed mainly medium to low ecological risks.

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ABSTRACT

Organic fertilizer or manure containing antibiotics has been widely used in organic farms, but the distribution and potential impacts of antibiotics to the local environment are not well understood. In this study, four quinolone antibiotics in soil samples ($n = 69$) from five organic vegetable farms in a subtropical city, Southern China, were analyzed using high performance liquid chromatography–tandem mass spectrometry. Our results indicated that quinolone compounds were ubiquitous in soil samples (detection frequency > 97% for all compounds), and their concentrations ranged from not detectable to 42.0 μg/kg. Among the targets, enrofloxacin (ENR) was the dominant compound, followed by ciprofloxacin (CIP) and norfloxacin (NOR). The average total concentrations of four compounds in the soils were affected by vegetable types and species cultivated, decreasing in the order of fruit > rhizome > leaf vegetables. Moreover, the average concentrations of quinolone compounds (except ENR) in open-field soils were higher than those in greenhouse soils. The concentrations of quinolone antibiotics in this study were lower than the ecotoxic effect trigger value (100 μg/kg) proposed by the Veterinary Medicine International Coordination commission. Risk assessment based on the calculated risk quotients indicated that NOR, CIP, and ENR posed mainly medium to low risks to bacteria.

1. Introduction

Antibiotics have been used in large quantities for several decades as human and veterinary medicine, and husbandry growth promoters. Because antibiotics usually cannot be absorbed or metabolized completely in human or animal body, a portion of administered antibiotics have been excreted into environment constantly as parent compounds or metabolites (Jjemba, 2002; Sarmah et al., 2006). Among various antibiotics, quinolones are extremely effective antibacterial agents. Quinolones can enter environment mainly through the excretion of human and animals, as well as the direct discharge of aquaculture products (Andreu et al., 2007). Previous studies showed that quinolones were found in various manure (Zhao et al., 2010; Leal et al., 2012; Zhou and Kang, 2013). Extremely high concentration of norfloxacin (NOR) and enrofloxacin (ENR) was detected in chicken manure from China, with the respective maximum concentrations of 225 and 1420 mg/kg (Zhao et al., 2010). In addition, extensive use of quinolones has also led to their widespread in wastewater, sewage sludge, surface water (Watkinson et al., 2009; Jia et al., 2012; Dorival-Garcia et al., 2013), and even resulted in the resistance of quinolones in the environmental compartments above (Figueira et al., 2011; Zhu et al., 2013). Environmental contamination of quinolones is recognized as an emerging issue of concern to scientists and the public (Andreu et al., 2007). Recently, some studies have investigated the occurrences of quinolones in soils (Martinez-Carballo et al., 2007; Karci and Balcioglu, 2009; Hu

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et al., 2010; Li et al., 2011, 2013a, 2014a; Leal et al., 2012; de la Torre et al., 2012; Xie et al., 2012; Zhou et al., 2013). Different quinolones were frequently detected with the levels of μg/kg in the soils from Turkey, Brazil, China, and so on (Karci and Balcioglu, 2009; Li et al., 2011, 2013a; Leal et al., 2012). For example, Xie et al. (2012) reported that the concentrations of ciprofloxacin (CIP), ENR and NOR ranged from 0.10 to 288 μg/kg in the surface soil in a typical intensive vegetable cultivation area in Northern China. However, different from that study, the temperature and humidity are much higher in South than that in North China, which may increase the transportation, sorption and degradation of antibiotics in manure and manure-amended soil (Ötker and Akmehmet-Balcıoğlu, 2005; Wang et al., 2006; Stoob et al., 2007). Our previous study showed that quinolones were detected in the soils from different vegetable farms in Southern China (In China, vegetable farms are classed as traditional, pollution-free, green-food, and organic farmlands), and their highest concentrations were observed in the vegetable farms affiliated with livestock farms (Li et al., 2011). Nevertheless, Li et al. (2011) have not investigated the occurrence of quinolones in the soils from organic vegetable farms.

With the increasing demand for organic products, the public need to know the whole story related to the contamination with different pollutants in the soils of organic farms and their potential safety effects on the agricultural products. It is suspected that the residues of antibiotics in the soils of organic farms should be higher than that in conventional ones, due to the usage amount of organic fertilizers including manure in organic farms (Williams and Hedlund, 2013). CIP and tetracycline were detected in the soils from organic vegetable farms in Tianjin, Northern China (Hu et al., 2010). Despite the large consumption of antibiotics in China, the reports about the occurrence of antibiotics in organic vegetable farms are still very scarce. Thus, this study aimed to investigate the occurrence and distribution of quinolone antibiotics in the soils of organic vegetable farms in a subtropical city, Southern China, and to evaluate the potential ecotoxicological risk caused by quinolones.

2. Materials and methods

2.1. Chemicals and materials

Four quinolone antibiotics, including NOR, CIP, lomefloxacin (LOM) and ENR, were obtained from Dr. Ehrenstorfer-Schäfers (purities > 98%, Augsburg, Germany). HPLC-grade acetonitrile and methanol were obtained from Sigma-Aldrich (St. Louis, MO). All other reagents were of analytical grade, and water was of high purity.

Standard stock solution of quinolones (100 μg/mL) was prepared by dissolving 0.0100 g of the substances in 100 mL of acetonitrile:water (10/90, V/V, with 0.1% formic acid). It was kept in a brown glass vial which was stored in a refrigerator (4 °C). The stock solution was diluted using acetonitrile:water (10/90, V/V, with 0.1% formic acid) to get working solutions before use.

2.2. Sample collection

Guangdong province, a subtropical area located in Pearl River Delta region, Southern China, is one of the major vegetable production regions in China. In 2011, the sown area of vegetables in Guangdong was 1.209 million ha, and the output was 28.51 million tons (Wan, 2012). The sown area of vegetables in Guangzhou, the provincial capital of Guangdong, contributed 15.6% to that of Guangdong province (Wan, 2012), and the area of organic vegetable farms in Guangzhou was about 1916 ha (Vegetable Office of Bureau of Agriculture in Guangzhou, 2011). In this study, five large-scale organic vegetable farms in Guangzhou, namely farms PY, CH, HL, QX and XA, were selected for soil sampling (Table 1).

The areas of the five farms ranged from 13.3 to 1000.5 ha. Their annual agricultural products ranged from 1000 to 3000 tons which were exported to Japan, Canada, the United States, the European, Hong Kong and other countries or regions. In these farms, more than fifty vegetable species were cultivated, including leaf vegetables, melon or fruit vegetables, and root or stem vegetables. Only organic fertilizers including animal manure (cow manure, chicken manure, etc.) were applied in the process of production. And, groundwater was used for irrigation.

Soil samples ($n = 69$) were collected in November 2011. According to the technical guidance of environmental monitoring, the soil samples were collected avoiding vegetable field edge, crop roots and the sites just fertilized. Six to eight soil subsamples (depth 0–20 cm) were collected randomly from the field where each vegetable was cultivated, and then fully mixed to get one composite sample. The soil samples were picked into brown glass bottles and then transported to the laboratory immediately. The samples were stored in a refrigerator, and then air-dried and sieved (1 mm) before analysis. The main physical and chemical properties of soils were measured and the results based on a dry weight were as follows: 15.1 ± 0.5 g/kg of organic matter, 0.98 ± 0.06 g/kg of total nitrogen, 0.83 ± 0.03 g/kg of total phosphorus, 20.7 ± 1.01 g/kg of total potassium, and 4.69 ± 0.21 cmol/kg of cation exchange capacity, respectively.

2.3. Sample extraction and cleanup

The procedures of sample extraction and cleanup were conducted following the methods by Ho et al. (2012), with small modification. One gram of soil sample was placed in a 10 mL centrifuge tube and extracted with 5 mL of 50% $MgNO_3$ aqueous solution containing 4% aqueous ammonia. The tubes were vortexed (XW-80A, Haimen, China) for 10 min and extracted triplicately in an ultrasonic bath (KQ-250E, Kunsan, China) for 10 min. Then, the extracts were centrifuged (HC-3018, Hefei, China) at 4500 rpm for 5 min. The supernatants were concentrated to near dryness using a rotary evaporator (RE-2000, Shanghai, China), and then was purified by Oasis HLB extraction cartridges (3 mL/60 mg, Waters, USA).

The cartridge was conditioned with 6.0 mL of methanol, followed by 6.0 mL of Milli-Q water. The flow speed was set at 1.0 mL/min. The extracts were loaded onto the cartridges and then rinsed with 6 mL of Milli-Q water and dried for 5 min. The cartridges were eluted with 3 mL 1% acidified acetonitrile at a flow rate of 1.0 mL/min. The eluate was collected and concentrated under a gentle stream of nitrogen gas to about 0.1 mL, and then dissolved in 0.1% formic acid aqueous solution and 0.1% formic acid acetonitrile (90/10, V/V) to a final volume of 1.0 mL. The solution finally was filtered through 0.22 μm syringe filters (Tianjin, China) for instrument analysis.

Table 1
Characteristics of the five organic vegetable farms in Guangzhou, China.

Name of farms	Scale (hectare)	Irrigation water	Fertilization	Vegetable species
CH	1000.5	Groundwater	Swine manure, organic fertilizer	Leaf vegetables, melon vegetables
PY	66.7	Groundwater	Organic fertilizer	Leaf vegetables, melon vegetables, tuber vegetables
HL	13.3	Groundwater	Chicken manure	Leaf vegetables, tuber vegetables
QX	66.7	Groundwater	Organic fertilizer	Leaf vegetables, tuber vegetables
XA	33.4	Groundwater	Organic fertilizer	Leaf vegetables, melon vegetables

2.4. Instrument analysis

The measurement of quinolone antibiotics was conducted by a high-performance liquid chromatography–tandem mass spectrometry system (Alliance 1100 of HPLC, AB4000QTRAP of MS, Agilent) as methods described by previous studies (Tai et al., 2009; Lombardo-Agui et al., 2012). Chromatographic separation was achieved using an Agilent Eclipse Plus C18 column (5 μm, 2.1 × 150 mm). The mobile phase was acetonitrile:water (10/90, V/V, with 0.1% formic acid) at a flow rate of 0.2 mL/min. The column temperature was 20 °C, and the injection volume was 5 μL.

The instrument was operated in positive ion (ESI) mode for multiple reaction monitoring (MRM). The desolvation temperature was adjusted to 600 °C, ion source voltage was set at 5.5 kV, curtain gas was set at 0.14 MPa, atomizing air pressure was set at 0.41 MPa and dry gas pressure was set at 0.35 MPa. The collision pressure level was high. The details of instrument parameters are shown in Supplementary Table S1.

2.5. Quality assurance/quality control and data analysis

Blank spikes, method blanks (solvent), matrix spike duplicate and sample duplicates were routinely analyzed with field samples. The standard deviation of duplicate samples was less than 16.2%. The mean recoveries of four quinolone antibiotics in soils ranged from 67% to 88%. The correlation coefficients (R^2) of the calibration curve (0.5 to 100 μg/L) were >0.999, and the relative standard deviation (RSD) for all analytes was <11%. The limits of detection based on a signal-to-noise ratio of 3 (S/N > 3) ranged from 0.001 to 0.003 μg/L, and the limits of quantification ranged from 0.004 to 0.011 μg/kg.

The concentrations of quinolones in soils were reported on a dry weight basis. Statistical analysis including one-way analyses of variance (ANOVA) followed by Duncan (D) test were performed with *Microsoft Excel 2007* and *SPSS 17.0*. Statistical significance was set at $p < 0.05$.

3. Results and discussions

3.1. Concentrations and profiles of quinolone antibiotics in the soils

Four quinolone antibiotics were analyzed and the detection frequency was 97% for CIP and 100% for ENR, NOR, and LOM, respectively. The concentrations of individual compounds ranged from ND (not detectable) to 42.0 μg/kg (Table 2). Most of them were between ND − 1 μg/kg (42.3–73.2%) and 1–10 μg/kg (25.4–43.7%), and less than 20% of them were between 10 and 50 μg/kg (Table 2). The average concentrations of individual compounds ranged from 1.32 to 5.12 μg/kg, decreasing in the order of ENR (5.12 μg/kg) > CIP (3.91 μg/kg) > NOR (3.61 μg/kg) > LOM (1.32 μg/kg). The maximum concentration was 42.0 μg/kg for CIP. The total concentrations of four quinolones (∑QNs) in all samples varied from 0.46 to 55.2 μg/kg with an average value of 14.0 μg/kg (Table 2). About 40% of the ∑QNs were between 10 and 50 μg/kg, while about 30% of them were between 1 and 10 μg/kg or <1 μg/kg, respectively.

In comparison with the concentrations of quinolones in soils in the developed and developing countries (Rehman et al., 2013) (Table 3), the average concentrations of four quinolones as well as the ∑QNs in this study were significantly lower than those reported in the soil of Shandong province, Northern China (Xie et al., 2012; Li et al., 2013a), and those reported in our previous study about different kinds of vegetable farms (i.e., traditional, pollution-free, green-food vegetable farms) (Li et al., 2011), and also lower than those reported in other countries (Leal et al., 2012), but were comparable with those in the winter soil of an organic vegetable farm in Tianjin, Northern China (Hu et al., 2010). Moreover, both the concentrations of individual compounds and the ∑QNs in this study were lower than the ecotoxic effect trigger value (100 μg/kg) of veterinary medicine set by the International Coordinating Committee (Karci and Balcioglu, 2009), indicating the low ecological risk deriving from quinolones in this study.

In most studies, the interested compounds in soil were the four commonly used quinolones (NOR, CIP, ENR and LOM), and their concentrations were on the order of μg/kg with different detection frequencies (Table 3) (Martinez-Carballo et al., 2007; Karci and Balcioglu, 2009; Liu et al., 2010; Li et al., 2011, 2014a; Ho et al., 2012; Leal et al., 2012; Shi et al., 2012; Xie et al., 2012; Zhou et al., 2013). However, the profiles of quinolones varied greatly in different regions. For example, ENR was the dominate compound in soils from Brazil (Leal et al., 2012), while the concentration of CIP (106 μg/kg, mean) was one to five times higher than that of ENR (55.7 μg/kg) and NOR (18.6 μg/kg) in soils from Northern China (Xie et al., 2012; Li et al., 2013a).

It was contrary to our previous suspicion, antibiotic concentrations in soils from organic vegetable fields were not higher, but lower than those of the conventional farms, although three or more batches of vegetables were cultivated each year in our research area, indicating more receiving organic fertilizers or manure. Several studies have demonstrated the high levels of antibiotics in fertilizers or manure (Hu et al., 2010; Tai et al., 2011; Leal et al., 2012) (Table 3). As shown in Table 3, quinolone concentrations in poultry litters from Sao Paulo State, Brazil were up to several mg/kg (Leal et al., 2012) and the average concentrations of quinolones in swine and cattle manure in Guangdong province were between 88.6 and 204 μg/kg (fresh weight) (Tai et al., 2011). The relative low antibiotic concentrations in soils from organic vegetable fields can be explained by several reasons. The subtropical and marine climate of high moisture and high temperature in this study area played a key role in biodegradation of antibiotics in the soils. Additionally, fertilization practices (e.g., fertilizer types and doses) could influence on soil respiration and physic-chemical properties (Evanylo et al., 2008; Lopez-Lopez et al., 2012), which would affect the behavior and fate of quinolones in the soil. Furthermore, long-term fertilization with organic fertilizers including manure could increase the contents of organic matter in soil (Li et al., 2013b) and improve microbial composition and diversity (Kong et al., 2006; Thiele and Beck, 2005), which would enhance the degradation of organic pollutants. For example, the total concentration of 16 polycyclic aromatic hydrocarbons in the soils chronically fertilized with chemical fertilizer plus pig manure was significantly lower than that with only chemical fertilizer or without fertilization (Han et al., 2009).

3.2. Quinolones in the soils from different organic vegetable farms

The concentrations of four quinolone compounds varied considerably in the soils from different vegetable farms (Fig. 1). Among the five farms, the highest ∑QNs (35.0 μg/kg) was found in farm CH, which was two times or more higher than others (Fig. 1). The lowest ∑QNs was observed in farm PY (5.09 μg/kg). The profiles of antibiotics

Table 2
Concentrations (μg/kg, dry weight) of quinolone antibiotics in soils from organic vegetable farms.

Compounds	NOR	CIP	LOM	ENR	∑QNs
Detection frequency (%)	100	97	100	100	100
Minimum	0.14	ND [a]	0.02	0.02	0.46
Maximum	17.9	42.0	11.0	24.4	55.2
Mean	3.61	3.91	1.32	5.12	14.0
Median	1.10	1.01	0.32	2.44	8.20
Standard deviation	4.44	7.32	2.33	6.24	15.5
CV [b] (%)	123	187	177	122	111
Percentage distribution (%)					
<1.0 μg/kg	46.5	57.7	73.2	42.3	26.8
1.0–10 μg/kg	43.7	28.2	25.4	39.4	28.2
10–50 μg/kg	9.8	14.1	1.4	16.9	42.2
>50 μg/kg	0	0	0	1.4	2.8

[a] ND—not detectable.
[b] Coefficient of variation.

Table 3
Concentrations (μg/kg, dry weight) of quinolone antibiotics in different soil and manure of the literatures.

	NOR			CIP			LOM			ENR			References
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	
Different soil													
China (Guangzhou)	14.9	64.4	–	31.5	54.7	–	0.87	6.84	–	5.13	408	–	Tai et al. (2009)
China (Guangdong)	14.9	150	61.9	5.30	120	26.9	ND[b]	13.7	7.4	5.10	1348	99.4	Li et al. (2011)
China (Tianjin)		NA[a]		0.80	30.1	–		NA			NA		Hu et al. (2010)
China (Tianjin)	ND	86.9	10.2	ND	84.9	6.44	–	–	1.93	–	–	4.19	Shi et al. (2012)
China (Shandong)	0.40	288	55.7	2.40	652	106		NA		0.10	167	18.6	Xie et al. (2012); Li et al. (2013a, 2013b); Li et al. (2014a)
Turkey		NA		–	–	53.0		NA		13.0	204	–	Uslu et al. (2008)
Turkey		NA			ND			NA		20.0	60.0	50.0	Karci and Balcioglu (2009)
Malaysia		ND	95.7	–	NA			NA		36.1	378	–	Ho et al. (2012)
Brazil		ND			ND			NA		17.4	26.7	22.9	Leal et al. (2012)
Austria		NA			ND			NA		–	–	50.0	Martinez-Carballo et al. (2007)
Different poultry litters													
China (Guangzhou) (swine dungs)	ND	620	150	ND	1340	280	ND	950	200		NA		Guo et al. (2011)
China (Guangzhou) (chicken dungs)	ND	70.0	30.0	ND	230	80.0	ND	200	40.0		NA		Guo et al. (2011)
China (Guangdong) (swine dungs)[c]	1.2	262	131	20.8	647	153	0.6	226	101	1.9	595	197	Tai et al. (2011)
China (Guangdong) (cattle dungs)[c]	8.5	431	204	7.90	199	88.6	38.9	647	191	30.7	150	89.7	Tai et al. (2011)
China (Guangxi) (swine dungs)	–	–	47.9	–	–	9.08	NA	NA	NA	–	–	16.5	Zhou et al. (2013)
China (Guangxi) (cattle dungs)	–	–	63.4	–	–	7.62	NA	NA	NA	–	–	6.30	Zhou et al. (2013)
China (Tianjin) (organic fertilizers, chicken dungs)		NA		300	3000	–		NA			NA		Hu et al. (2008)
China (Tianjin) (organic fertilizers, chicken dungs)		NA		ND	4300	–		NA			NA		Hu et al. (2010)
Turkey		NA			ND			NA		–	–	60	Karci and Balcioglu (2009)
Malaysia	30.7	1886	–		NA			NA		112	26,863	–	Ho et al. (2012)
Brazil	800	4550	2550	650	2130	1370		NA		390	30,970	6680	Leal et al. (2012)
Austria		NA			ND			NA		–	2.80	–	Martinez-Carballo et al. (2007)

[a] NA: not available.
[b] ND: not detectable.
[c] Concentrations expressed based on a fresh weight.

were also different in five farms. For example, NOR, CIP and ENR were the dominant compounds in farm CH (accounting for 86.4% of the $\sum$QNs), NOR and CIP were the dominant compounds in farm QX (80%) and ENR was the dominant compound in farm HL (69.3%), respectively. The concentration of LOM was always the lowest in the soils of five farms. The distribution pattern of antibiotics in this study was different from that in a vegetable farm of Shandong province, Northern China, which was dominated by CIP (Xie et al., 2012; Li et al., 2014a).

The variation of quinolone concentrations in different organic vegetable farms could be attributed to fertilization practices, vegetable planting models, planting age, and elevation (Li et al., 2013a). In farm CH, both swine manure and commercial organic fertilizers were applied to the soil, while in other farms only commercial organic fertilizers were applied. The concentrations of quinolones in swine manure were higher than those in cattle manure from both Guangdong province (Tai et al., 2011) and Guangxi province (Zhou et al., 2013), which explained the relative higher concentrations of quinolone in farm CH than others. Moreover, the organic fertilizers or manure were applied differently according to the vegetables planted. In Guangzhou, three or more batches of vegetables were cultivated each year. The planting models of vegetable types could be classified into "leaf–fruit–leaf vegetable," "leaf–melon–leaf vegetable," "rhizome–melon-leaf vegetable," "rhizome–leaf–melon vegetable," and so on. Li et al. (2013a) reported that vegetable planting model was a major factor for the spatial stratification of quinolones in soil. In addition, planting ages (the years with continuous vegetable cultivation) varied greatly among the five farms. Farm PY has the longest history which was established in 1994, and farms CH and QX were established in 2003 and 2000, respectively. The planting history associated with fertilization practices affected the residues of quinolones in soil (Golet et al., 2003; Pusino et al., 2003; Li et al., 2013a).

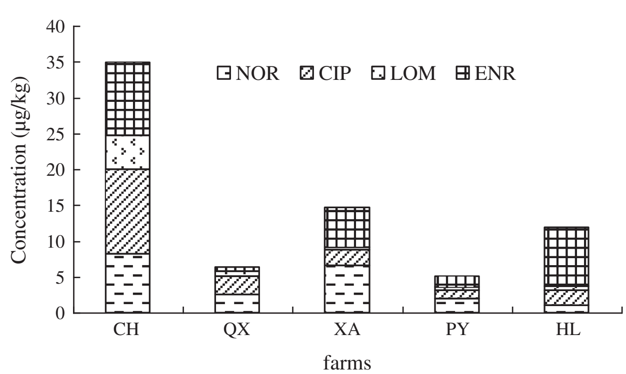

Fig. 1. Average concentration distribution of quinolone antibiotics in soils from different vegetable farms.

3.3. Quinolones in the soils growing different vegetables

The mean $\sum$QNs in the soils growing different types of vegetables were different considerably, decreasing in the order of fruit vegetables (44.8 μg/kg) > rhizome vegetables (37.0 μg/kg) > leaf vegetables (32.1 μg/kg) (Fig. 2a). In the soils growing fruit vegetables, the average

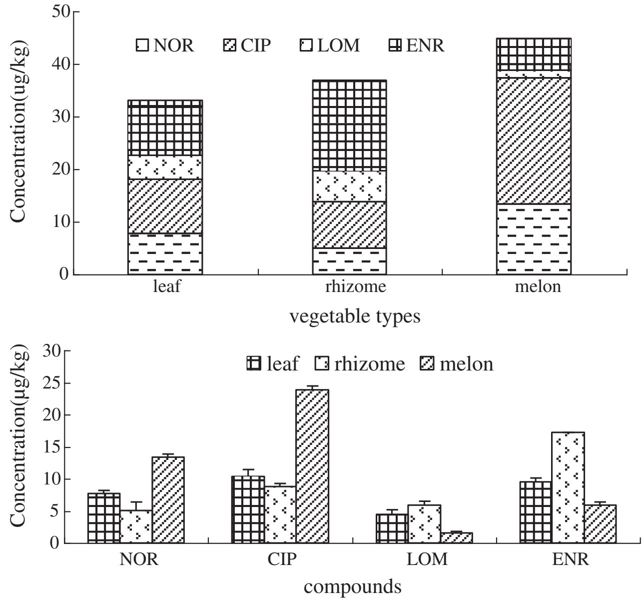

Fig. 2. Average concentration distribution of quinolone antibiotics in soils cultivated different types of vegetables.

concentration of CIP (23.9 μg/kg) was high, while the average concentrations of the other three quinolones decreased sharply in the order of NOR (13.4 μg/kg) > ENR (6.00 μg/kg) > LOM (1.60 μg/kg) (Fig. 2b). In the soils growing rhizome vegetables, ENR was a predominant compound with a mean concentration of 17.2 μg/kg, and the average concentrations of the other three quinolones were all less than 10 μg/kg. Differently, in the soils growing leaf vegetables, the average concentrations of CIP (10.3 μg/kg), ENR (9.51 μg/kg) and NOR (7.77 μg/kg) were all comparable, which were much higher than that of LOM (4.51 μg/kg).

Additionally, the occurrences of quinolones in soils were also affected by vegetable species planted. In this study, the vegetable species planted were different among the five farms. For example, during sampling period (November of 2011), twenty vegetable species could be harvested in farm PY, while only six in farm HL. In farm CH, the $\sum$QNs in the soils growing different vegetables varied from 15.0 to 35.2 μg/kg, and the highest value was observed in the soil growing Late Chinese flowering cabbage, followed by eggplant and ginger (Fig. 3). The predominant compounds in the soils growing various vegetables were different. For example, CIP was the most abundant compound in the soils planting late Chinese flowering cabbage and eggplant, while NOR and ENR dominated in the soils growing sweet potato, ginger, mini Chinese cabbage and carrot (Fig. 3).

The distribution differences of quinolones in the soils growing various vegetables might be related to fertilization practice, vegetable uptake and rhizospheric degradation. The quantity of fertilizers used in soils was associated with the vegetables planted. The longer growth period of vegetables was, the greater fertilizer quantity was applied. For instance, in farms PY and CH, the quantity of organic fertilizers (including manure) applied was about 15 t/ha for fruit or rhizome vegetables and 4.5–7.5 t/ha for leaf vegetables, respectively. The residual concentrations of $\sum$QNs in the soils growing eggplant, ginger and carrot were higher than those of lettuce and mustard seedlings (Fig. 3). The antibiotic compounds in soils could be taken up and transported by living plants via mass flow and through active uptake (Eggen et al., 2011; Li et al., 2014a). For example, Eggen et al. (2011) found that the uptake pattern of tested pharmaceuticals varied in carrot, barley, meadow fescue, wheat and turnip rape. Li et al. (2014a) reported that the residual concentrations of CIP, NOR and ENR in vegetables ranged from 2.0 to 658 μg/kg. But the uptake and accumulation of antibiotics by different plant species were different. For instance, the average NOR concentration in spinach was two times higher than those in tomato and cucumber as well as crown daisy, and concentrations of NOR in different vegetables were significantly higher than those of CIP and ENR (Li et al., 2014a). The average accumulation factors or bioconcentration factors (defined as quinolone concentration ratio of vegetables to the soils themselves growing) for NOR were between 1.47 (spinach) and 8.44 (tomato) (Li et al., 2014a). Furthermore, the enhanced degradation of organic pollutants by different plants in rhizosphere varied greatly (Cai et al., 2008; Mo et al., 2008; Li et al., 2014b). The different accumulation, translocation, and enhanced degradation by various plant species could lead to different removal of quinolones from soils.

3.4. Quinolones in the soils of open field and greenhouse

In Guangdong province as well as the other regions of China, vegetables are planted in two different cultivation systems: open field (conventional cultivation) and greenhouse (protected cultivation). In this study, both cultivation systems are used in farms CH and PY. The concentrations of quinolones in the soils of open field and greenhouse were different considerably. The average $\sum$QNs in the soils of open field (15.2 μg/kg) was higher by 28.8% than that of greenhouse (11.8 μg/kg) (Fig. 4). For individual quinolone compounds, their concentrations (except ENR) in the soils of open field were greater than those of greenhouse by 22.8–141%. The average concentrations of ENR, CIP and NOR in open-field soil were approximately 4.5 μg/kg, while in the soils of greenhouse, the average concentrations of ENR, NOR, CIP, and LOM were 5.07, 3.36, 2.64 and 0.71 μg/kg (Fig. 4), respectively.

Some studies have been conducted to compare the residues of heavy metals and pesticides in vegetables or soils between open field and

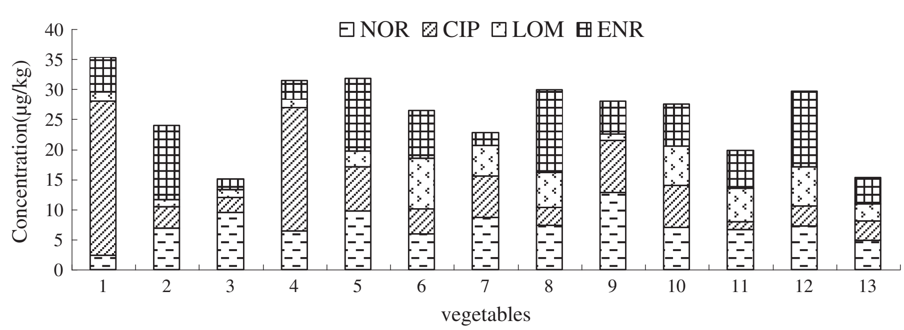

Fig. 3. Average concentrations of quinolone antibiotics in the soils growing various vegetables in farm CH. Bars corresponding to vegetables: 1—late Chinese flowering cabbage; 2—sweet potato (leaves); 3—lettuce seedling; 4—eggplant; 5—ginger; 6—garlic; 7—mustard; 8—mini Chinese cabbage 9—ash melon; 10—Chinese flowering cabbage; 11—mustard seedling; 12—carrot; 13—Chinese cabbage.

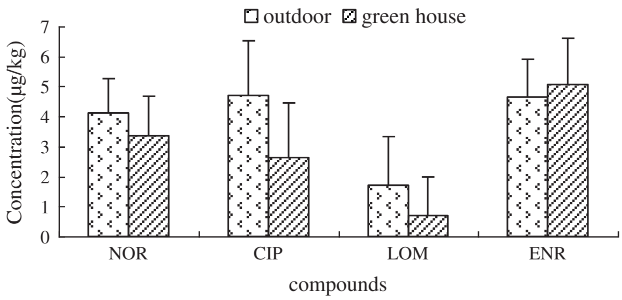

Fig. 4. Concentration distribution of quinolones in soils from differently cultivated conditions.

greenhouse (Li et al., 2008; Maia et al., 2009; Bojacá et al., 2013). It was reported that the concentrations of heavy metals (including Cr, Ni, Cu, As, Cd and Zn) and pesticides in greenhouse soils were obviously higher than those in open-field soils (Li et al., 2008; Wu et al., 2013a), while no difference of pesticide residues in tomatoes was found between greenhouse and open field (Bojacá et al., 2013). However, by far, reports on the residual distribution of antibiotics in different cultivation conditions are limited (Maia et al., 2009; Li et al., 2013a). Li et al. (2013a) reported that ENR, CIP, and NOR were all detected in greenhouse soils. Maia et al. (2009) reported that the residues of tetracycline in soils between greenhouse and open field were not obviously different, mainly because tetracycline was not derived from the manure fertilization, but acted as an insecticide sprayed on tomatoes.

As well known, the density of cultivation, the usage of fertilizers (including manure) and pesticides were different between greenhouse and open field (Marucci et al., 2011; Zhang et al., 2012; Li et al., 2013a), which caused different loss and residue of water, nutrients, or pesticides in soils (Marucci et al., 2011). The contents of organic carbon, total nitrogen, soluble organic nitrogen, cation exchange capacity, etc., in greenhouse were greater than those in open field (Ge et al., 2010; Zhang et al., 2012; Wang et al., 2013). Moreover, the soil activities (including microbial biomass nitrogen, sucrase and alkaline phosphatase activities, etc.) in greenhouses were more frequent than those in open field (Ge et al., 2010; Wu et al., 2013a). Additionally, the atmospheric temperature in greenhouse is higher than that in open field. These factors could result in differences in organic pollutants sorption to soil and degradation by microorganism between greenhouse and open field (Li et al., 2013a; Wu et al., 2013a), and finally led to the difference of pollutant dissipation. In this study, subtropical and marine climate conditions with high moisture and high temperature in Guangzhou especially in greenhouse caused much lower residues of quinolones in soils than in the other areas.

3.5. Risk assessment

The risk of contaminants in the environment can be evaluated by means of risk quotient (RQ) values. The RQ values are generally expressed as the ratio of the measured environmental concentrations (MEC; or predicted environmental concentrations, PEC) to the predicted no-effect concentrations (PNEC) for the specific pollutants (European Commission, 2003).

Following the European technical guidance document on risk assessment (European Commission, 2003), PNEC values are derived from acute toxicity or short-term data (i.e., Lethal Concentration, LC; Effect Concentration, EC; and No-Observed Effect Concentration, NOEC) divided by an assessment factor (Martin et al., 2012a,b; Zhang et al., 2013). However, the studies about the toxicity of antibiotics have been estimated mainly for the aquatic environment using fish, algae, bacteria, etc., as bioreporters (Halling-Sorensen et al., 2000; Isidori et al., 2005; Gonzalez-Pleiter et al., 2013), and very few study has reported the risks to the terrestrial compartment (particularly to the soil) (Gao et al., 2008). Thus, calculating the RQ values was a challenge due to the lack toxicities of quinolones in soils and the difficulty in estimating the $PNEC_{soil}$.

Nevertheless, an equilibrium partitioning method was recommended to estimate the toxicity of contaminants in soil, based on the assumption that bioavailability, bioaccumulation, and toxicity were closely related to the pore water concentrations (European Commission, 2003; Martin et al., 2012a, 2012b). In this study, the $PNEC_{soil}$ values were estimated from $PNEC_{water}$ values through the equilibrium partition approach as the following equation (European Commission, 2003; Martin et al., 2012a,b):

$$PNEC_{soil} = PNEC_{water} \times K_d \quad (1)$$

where K_d is the soil–water partition coefficient. $PNEC_{water}$ values were generally calculated based on the lowest acute toxicity data reported in literatures and using an assessment factor of 1000 which takes into account inter-species variations (European Commission, 2003; Martin et al., 2012a,b).

$PNEC_{water}$ values in the present study were calculated using the estimated toxicity data of quinolone antibiotics for non-target organisms (details in Supplementary Table S2) and the $PNEC_{soil}$ values were estimated in Eq. (1) (Table 4). Additionally, the RQ values for quinolone compounds were calculated using the MEC in the soils (Table 2) and the $PNEC_{soil}$ values, and the RQs were presented in Fig. 5. A commonly accepted ranking criterion was applied, according to European Commission (2003) and Verlicchi et al. (2012), namely $RQ < 0.1$ low risk; $0.1 \leq RQ < 1$, medium risk; and $RQ \geq 1$, high risk. In this study, the RQ values ranged from 2.0×10^{-4} to 1.64 (Fig. 5a). It was found that both CIP and ENR posed high risks to bacteria, although it occurred only in 2.90% and 1.45% of the soil samples (Fig. 5b). NOR, CIP, and ENR caused medium risks to bacteria in 34.8%, 33.3% and 49.3% of the soil samples, respectively (1.45% for LOM). Obviously, the four quinolone compounds in most of the soil samples posed just low risks to bacteria (Fig. 5).

However, it is worth to notice that the risk assessment in this study was estimated following the toxicity data of bacteria. The risk levels might be overestimated or underestimated, because the joint effects of various quinolone compounds were not considered (Backhaus and Faust, 2012). Additionally, scientists reported that earthworm (*Eisenia fetida*) not only could grow normally in quartz sands spiked with CIP solution of 100 μM CIP (being equal to 33.1 mg/kg), but also could accumulate and eliminate CIP, even could highly increase CIP mineralization in soils (with CIP concentrations of 50–250 μg/kg) (Wen et al., 2011; Mougin et al., 2012). Similarly, no significant effect was observed on the growth rates of earthworms (*E. fetida*) and catalase activity after exposed to ENR (at 500 mg/kg) for 14 days (Gao et al., 2008). Taking these results into account, CIP and ENR posed very low risks. Nevertheless, the quinolone residue in the soils needs to be concerned, because quinolones could be taken up and accumulated by vegetables (Wu et al., 2013b; Li et al., 2014a), which could pose a potential risk to human health, and quinolones resistance could develop in the contaminated soils (Girardi et al., 2011; Zhu et al., 2013). Additionally, as described above, four quinolone compounds were detected in all the soil samples of the five organic vegetable farms (except CIP in three samples), thus their joint toxicity should not be ignored (Cleuvers, 2004).

4. Conclusions

The residues of quinolone antibiotics were widely detected in the soils from organic vegetable farms in Guangzhou, Southern China. The concentrations of individual compounds and their total concentrations ranged from ND to 55.2 μg/kg, being less than the ecotoxic effect trigger value (100 μg/kg) set by the Steering Committee of Veterinary International Committee on Harmonization. Due to the high temperature and moisture in the research area, the levels of quinolone antibiotics in the soils from organic vegetable farms, particularly greenhouse, were

Table 4
Predicted no-effect concentrations (PNEC) and the most sensitive species to quinolone antibiotics.

Compounds	Species	Toxicity	Ecotoxicity (mg/L)	$PNEC_{water}$ (μg/L)	LogK_d	$PNEC_{soil}$ (μg/kg)	Reference
NOR	Luminescent marine bacteria (*V. fischeri*)	Bioluminescence inhibition, 24 h	EC_{50} = 0.022	0.022	3.13[a]	29.68	Backhaus et al. (2000)
CIP	Cyanobacterium (*Microcystis aeruginosa*)	Growth, 72 h	EC_{50} = 0.005	0.005	3.71[b]	25.64	Halling-Sørensen et al. (2000)
LOM	Luminescent marine bacteria (*V. fischeri*)	Bioluminescence inhibition, 24 h	EC_{50} = 0.022	0.022	3.63[c]	93.85	Backhaus et al. (2000)
ENR	Cyanobacterium (*Microcystis aeruginosa*)	Growth, 5d	EC_{50} = 0.049	0.049	2.69[d]	24.00	Pobinson et al. (2005)

[a] Data from Gong et al. (2012).
[b] Data derived from the mean of data reported by Conkle et al. (2010), Picó and Andreu (2007), Leal et al. (2012), and Golet et al. (2003).
[c] Data derived from the mean of the data reported by Picó and Andreu (2007), Leal et al. (2012), and Golet et al.(2003).
[d] Data derived from Uslu et al. (2008).

relatively low, even though the farms were chronically fertilized with organic fertilizers including manure. The distribution patterns of quinolones in the soils were associated with different farms and species of vegetables planted. NOR, CIP, and ENR posed mainly medium to low risks to bacteria. Considering the potential accumulation of quinolone antibiotics by vegetables from the soils, further research should assess the human exposure to antibiotics via plant-derived food. Moreover, the eco-toxicity of antibiotics and its resistance in organic vegetable farms are needed to be investigated.

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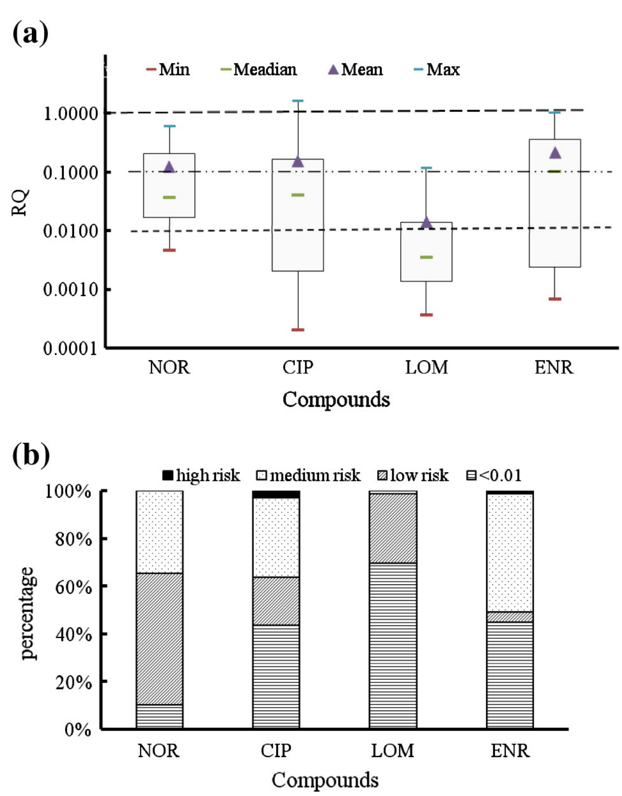

Fig. 5. Calculated risk quotients (a) and percentage (b) of quinolone antibiotics in the soils from different vegetable farms.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2014.04.015.

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