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Spatial estimation of antibiotic residues in surface soils in a typical intensive vegetable cultivation area in China

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ABSTRACT

Antibiotic residues in surface soils can lead to serious health risks and ecological hazards. Spatial mean concentration of antibiotic residues in the soil is the most important indicator of a region's environmental risk to antibiotic residues. Considerable estimation error would lead to an inefficient strategy of pollution control that happens when sample size is small and the estimation model does not match the spatial features of the object to be surveyed. On the basis of the available datasets, it was found that the distribution of antibiotics residue in soil follows a spatial stratification pattern. Accordingly, we used a new spatial estimation method called Mean of Surface with Non-homogeneity (MSN) to estimate antibiotic concentrations in surface soil of the Shandong Province, an important vegetable growing region in China. The standard error of the mean estimates obtained by MSN was significantly smaller (by about 1.02–6.82 μg/kg) than the estimation errors produced by three mainstream methods, simple arithmetic estimation (2.9–11.8 μg/kg), stratified estimation (2.5–10.6 μg/kg) and ordinary kriging estimation (2.2–8.2 μg/kg).

1. Introduction

Veterinary antibiotics are widely used to treat disease and protect animal health worldwide. They are also incorporated into animal feed to improve growth rate and feed efficiency (Li et al., 2011; Sarmah et al., 2006; Sukul and Spiteller, 2007). Antibiotics are poorly adsorbed in animal guts, resulting in about 30–90% of the parent compound excreted unchanged in feces and urine (Alcock et al., 1999; Aust et al., 2008; Halling-Sørensen et al., 1998; Sarmah et al., 2006). Some antibiotics remain biologically active after they enter the environment (Sarmah et al., 2006). Using animal waste as fertilizer is a common practice in many countries (Zhao et al., 2010). Antibiotic residues used in animal husbandry enter the soil by means of manure (Jjemba, 2002; Karci and Balcioglu, 2009). In these cases, residue accumulation can damage the structure of bacterial communities, be absorbed by crops threatening the safety of agricultural products, or be leached to groundwater affecting environmental health (Hirsch et al., 1999; Martínez-Carballo et al., 2007).

The spatial mean concentration of antibiotic residues in the soil is the most critical parameter in the evaluation of potential human and environmental risks (Karci and Balcioglu, 2009; Sukul and Spiteller, 2007). Inaccurate mean estimation of the antibiotic residues in soil will lead to considerable bias in risk assessment. There are various possible factors that may affect the accuracy of mean concentration estimates, including sampling and instrumental errors as well as errors linked to the estimation method itself. It is worth noticing that the error associated with the specific estimation method is often overlooked in practice.

Several methods have been used to estimate mean soil pollutant concentrations, such as random sampling, ordinary kriging (OK) and stratification (Li et al., 2008; Modis et al., 2008; Saito et al., 2005). The suitability of each method depends on the spatial characteristics of the antibiotic-soil system; e.g., when surface soil samples are considered that are randomly drawn across space the corresponding antibiotic mean should offer unbiased pollutant concentration estimates (Stehman et al., 2003). When the pollutant surface is spatially homogeneous (constant mean and variance across space), the OK generates estimates that are unbiased and satisfy the minimum error variance criterion (Bishop and McBratney, 2001; McGrath et al., 2004). However, due to the physical heterogeneity of pollutants, the limited number of in situ samples and the varying importance of different

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parts of the area of interest, the assumptions of sampling randomness and surface homogeneity often are not satisfied in practice (Christakos, 1985; Li et al., 2008; Wang et al., 2009). Instead, the surface mean and variance change across space. Some surface non-homogeneity features may be handled by incorporating a trend model in the OK method. However, other non-homogeneous features neither can be filtered out by a spatially continuous trend model nor can be represented adequately in terms of adaptive variograms (Wang et al., 2009). In fact, stratified non-homogeneity is one of these surface features in which the variograms of surface strata (sub-areas) exhibit considerable differences.

For surfaces with stratified non-homogeneity as above, Wang et al. have proposed the so-called Mean of Surface with Non-homogeneity (MSN) method (Wang et al., 2009). The MSN method combines the merits of spatial stratification with those of OK optimal estimation to generate estimates of pollutant means and variances across space (Hu and Wang, 2011). In this way, MSN provides the best linear unbiased estimator (BLUE) of the actual concentration (Wang et al., 2009); and it considers non-homogeneous surfaces that are converted to several homogeneous sub-surfaces by means stratification (Wang et al., 2010b). The latter is a commonly encountered situation in the real world.

Due to food safety issues, antibiotic contamination is an urgent problem in regions of organic vegetable production (Hu et al., 2010; Siderer et al., 2005). Antibiotic residue levels in soil are closely related to the usage, soil type, and physico-chemical properties of the antibiotics. This results in a stratified non-homogeneous antibiotic distribution in soil, which can be estimated by MSN, and then compared with commonly used techniques of simple random statistics, stratified statistics, and geostatistical OK. Accordingly, the objective of the present study is to use the MSN method to derive BLUE estimates of the spatial distribution of antibiotic residues in surface soils of the Shandong Province, which is an important vegetable growing region in China. Fluoroquinolones (FQs) constitute a group of widely prescribed antibiotics and have been frequently used in both human and veterinary medicine due to their broad-spectrum antibacterial features. They have a longer high-life (DT_{50}) than other general veterinary antibiotics (>6 months following application) (Boxall et al., 2006). Since these compounds residues could persist in the soil environment for a long time, they were selected as target antibiotics in the present study.

2. Materials and methods

2.1. Reagents and sampling

Ciprofloxacin (CFX), enrofloxacin (EFX) and norfloxacin (NFX) were purchased from Sigma (St. Louis, MO, USA). Acetonitrile and methanol (HPLC grade) were purchased from Fisher (New Jersey, USA). Water was purified in a Milli-Q system (Millipore, Bedford, MA, USA). Oasis HLB (200 mg, 6 ml) cartridges for hydrophilic–lipophilic balances and SAX cartridge (200 mg, 3 ml) were purchased from 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 with a concentration level of 100 μg/ml and stored at temperature of −20 °C for about a week.

As noted earlier, the study domain is an important vegetable growing region located in the north-central part of the Shandong Province (China). The study region covers an area of about 160 km^2 and was selected for its multiform and representative planting types. The main vegetable types grown in the region are cucumber, tomatoes, peppers, melons, and eggplant. Animal manure (chicken manure, cow dung, etc.) has been used as organic fertilizer for several years. For the purpose of the present study, a total of 100 soil samples were systematically collected from the region of interest (Fig. 1). The average distance between sample locations was approximately 1 km. Using a small shovel, soil samples were collected 0–15 cm below the soil surface during November 2010. Five sampling sites were distributed along an S-shaped path within each greenhouse and then fully mixed into a single sample. The samples were immediately transported to a laboratory for analysis under cooled conditions.

2.2. Sample analysis

The concentrations of fluoroquinolones (ciprofloxacin, enrofloxacin, and norfloxacin) in soil were analyzed using high-performance liquid chromatography and fluorescence detection(HPLC-FD). Lyophilized soil (1.0 g) was extracted by 5 ml potassium phosphate buffer with acetonitrile (V:V = 1:1) and sonicated for 15 min. After that, centrifuge tubes were centrifuged at 3000 ×*g* in air-cooled conditions. The extraction procedure was performed 3 times and the supernatants were combined. Oasis HLB (200 mg, 6 ml) and SAX cartridge (200 mg, 3 ml) were obtained from Waters Corporation (Milford, MA, USA) and Bonna-Agela Technologies (Tianjin, China). Each cartridge was sequentially preconditioned with 6.0 ml methanol and 6.0 ml Milli-Q water. The mixture extraction solution with organic reagent under <5% was loaded onto the cartridge at a flow rate of approximately 2 ml min^{-1}. The cartridge was then rinsed with 6 ml of Milli-Q and lyophilized for 40 min. Elution of the antibiotic compounds from the cartridges was done with 6 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. Agilent 1100 series HPLC system equipped with a fluorescence detector was used to analyze FQs at an excitation wavelength of 280 nm and an emission wavelength of 450 nm with a 20 μl injection volume. The mobile phase consisted of acetonitrile and 0.01 mol/L oxalic acid (80:20 V/V) at a 1 ml/min flow rate. Procedural blanks consisting of ultrapure water were analyzed as a control of procedural contamination. The method of standard addition was used to ensure identification of the target antibiotics in soil samples. Their respective recoveries of CFX, EFX, and NFX were about 71–82%, 68–85%, 65–87% in soil samples. External calibration curves were constructed by preparing the standard solutions at six known concentrations (0.01–1.0 mg/kg for FQs). Concentrations of the analytes in sample matrices were determined by using peak areas which corresponded to the unknown concentrations in the calibration curve. The detection limits of the three antibiotics were lower than 0.1 μg/kg, and the relative standard deviation (RSD) was in the range of 2.5–5.0%. Noticeably, fluoroquinolones (FQ) were detected in all soil samples.

2.3. Mean of surfaces with non-homogeneity (MSN)

The MSN method decomposes a non-homogeneous surface into smaller subsurfaces (strata) that are homogeneous, exhibiting minimum dispersion variances within strata and maximum dispersion variances between strata (Wang et al., 2009). Strata were formed on the basis of prior knowledge, pre-sampling, an effective proxy variable, and the distribution of other variables that are known to affect pollutant concentration (Rodeghiero and Cescatti, 2008; Wang et al., 2010a). The study region was stratified into 5 strata according to plant type. The plant type (vegetable species) determined the usage of fertilizer, and indirectly determined the antibiotics residues in surface soil. The main plant type of substrata 1, 2, 3, 4 and 5 was cucumber, tomato, chilies, muskmelon, and eggplant, respectively. Subsequently, the spatial mean of the pollutant surface and its variance were calculated by the MSN method that combined OK and stratified sampling. MSN is calculated by the free downloadable software: www.sssampling.org/MSN.

2.4. Data analysis

The exploratory analysis of FQ data was based on descriptive statistics techniques. A nonparametric Kolmogorov–Smirnov (K-S) test was used to test the normality of sample distributions. Also, a nonparametric Kruskal–Wallis (K-W) test was used to compare the residue values of each antibiotic among strata with the significance level

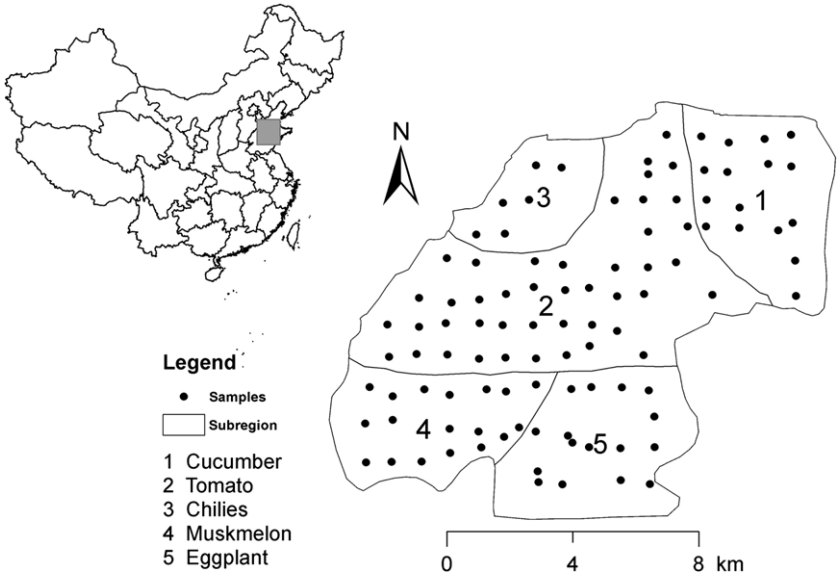

Fig. 1. Geographical location of the study region and the spatial sampling network.

set at $p<0.05$, which is suitable for comparisons between different datasets with uneven sample numbers (Yang et al., 2009; Zhao et al., 2010). Exploratory FQ analysis was carried out using the commercial software SPSS 13 for windows. Geostatistics (Helwade and Subramanyam, 2010; Saito et al., 2005) was used to describe the spatial variation (spatial dependence) of antibiotics in surface soil. The relevant computations were carried out using the GStat software (Pebesma, 2004; Pebesma and Wesseling, 1998). The study of the stratified non-homogeneous pollutant surfaces was done using MSN spatial sampling optimization (Hu and Wang, 2011).

As mentioned earlier, in order to evaluate the precision of MSN pollutant estimation, both the stratified random statistics and OK methods were used to calculate spatial averages of antibiotics at randomly re-sampling rates of 30, 50 and 70% of the original sample (see below). The relative performance of the different methods was then evaluated in terms of mean squared pollutant estimation errors.

3. Results and discussions

3.1. Descriptive statistics

The concentrations of ciprofloxacin (CFX), enrofloxacin (EFX) and norfloxacin (NFX) in the surface soil ranged between 2.4–651.6 μg/kg, 0.10–166.9 μg/kg, and 0.4–288.3 μg/kg, respectively. The detection frequency of CFX, EFX and NFX was 100%, 85% and 100%, respectively. The relevant statistics of the CFX, EFX and NFX concentrations are summarized in Table 1. CFX had the highest mean concentration (105.8 μg/kg), and EFX had the lowest mean concentration (18.6 μg/kg). The CV of the three antibiotics was greater than 100%. Low CV values indicated a spatially homogeneous distribution of soil variables, whereas high CV values indicated a non-homogenous surface distribution in the study area (Karanlik et al., 2011). The results of the K-S test ($p<0.05$) implied that the three antibiotics were not normally distributed. In such cases, the geometric mean or the transformed mean (log transformed or Box–Cox transformed) are used to describe average concentrations (McGrath et al., 2004). In the present study, following a Box–Cox transformation the results successfully passed the K-S test for normality. Note that the Box–Cox means of CFX, EFX and NFX were 62.3, 8.2 and 37.4 μg/kg, respectively, which were significantly lower than the corresponding arithmetic means (AM).

Table 2 shows the results of K-W testing differences in the three antibiotic residue levels between the five strata ($p<0.05$). The mean rank of CFX ranges from 31.6 to 77.1 μg/kg, 34.4 μg/kg to 60.1 μg/kg for EFX, and 41.4 μg/kg to 69.4 μg/kg for NFX. For all FQ, the strata 1 had the highest residue levels, and strata 4 had the lowest residue levels. For all FQ the K-W test results were below 0.05, indicating that statistically significant differences indeed existed for each FQ within strata. Plant type-based stratification was confirmed, which demonstrated the spatial heterogeneity of FQ residue levels.

Table 1
Descriptive statistics of NFX, CFX and EFX concentration (μg/kg) in surface soil.

FQ	DF	Mean	B-C	SD	CV (%)	Range	Q1	Q2	Q3	K-S
CFX	100%	105.8	62.3	118.3	111.8	2.4–651.6	28.9	75.2	141.5	<0.01
EFX	85%	18.6	8.2	26.7	143.3	0.1–166.9	2.7	8.3	22.3	<0.01
NFX	100%	55.7	37.4	56.4	101.2	0.4–288.3	14.2	33.3	79.5	<0.01

DF, detection frequency; B-C, Box–Cox mean; SD, standard deviation; CV, coefficient of variation; Q1, first quartile; Q2, median; Q3, third quartile.

3.2. Spatial pattern

The experimental variograms of soil FQ concentrations were calculated and different models were fitted to the raw variogram data: a spherical model for CFX and NFX, and an exponential model for EFX. The variogram model parameters are listed in Table 3. The ratio of nugget effect (C_0) over sill (C_0+C), $r=\frac{C_0}{C_0+C}$, can be used to express spatial correlations of soil variables (Cambardella et al., 1994; Chien et al., 1997; Zheng et al., 2008). If the ratio did not exceed 25%, i.e. $r\leq 25\%$, the FQ concentrations were considered strongly spatially dependent; if the ratio was between 25–75%, i.e. $25\%<r\leq 75\%$, the concentration was considered moderately spatially dependent;

Table 2
K-W strata tests of NFX, CFX and EFX concentrations in surface soil.

Strata	CFX		EFX		NFX	
	Samples	Mean rank	Samples	Mean rank	Samples	Mean rank
1	16	77.1	16	60.1	16	69.4
2	44	46.3	35	38.1	44	43.5
3	6	70.5	6	51.0	6	59.7
4	18	31.6	12	34.4	18	41.4
5	16	40.9	16	40.1	16	57.7
K-W test	Chi-sqr	Significance	Chi-sqr	Significance	Chi-sqr	Significance
	26.68	0.00	11.40	0.02	12.69	0.01

Table 3
Parameters of variogram models at the strata and site (global) scales.

	Scale	Variogram model	Nugget C_0(m)	C (m)	C_0/C_0+C	Spatial range (m)	R^2
CFX	Site	Spherical	6000	8500	0.41	5000	0.51
	Stratum 1	Spherical	3000	9000	0.25	1600	0.24
	Stratum 2	Spherical	7200	12300	0.37	3200	0.08
	Stratum 4	Spherical	6000	10000	0.38	2400	0.58
	Stratum 5	Spherical	1500	1500	0.50	2000	0.13
EFX	Site	Spherical	400	250	0.62	3200	0.07
	Stratum 1	Spherical	150	750	0.17	2400	0.52
	Stratum 2	Spherical	200	900	0.18	3600	0.26
	Stratum 4	Spherical	150	150	0.50	1800	0.03
	Stratum 5	Spherical	200	400	0.33	1600	0.16
NFX	Site	Exponential	1935	1936	0.50	5100	0.59
	Stratum 1	Spherical	1500	2100	0.42	2200	0.30
	Stratum 2	Spherical	1400	900	0.61	3200	0.33
	Stratum 4	Spherical	400	900	0.31	2000	0.53
	Stratum 5	Spherical	2200	3300	0.40	1600	0.06

and if the ratio was greater than 75%, i.e. $r>75\%$, the concentration was considered weakly spatially dependent (Sun et al., 2003).

In the present study the ratios of the three FQ varied from 0.41 to 0.62, showing moderate spatial dependence. Among the three FQ, the CFX distribution exhibited the highest spatial correlation. The three FQ showed relative high nugget effects, which indicates that spatial variation existed at ranges shorter than the minimum sampling interval. Moreover, the FQ ranges differ from each other. In particular, CFX and NFX had relative longer ranges than EFX. Since all FQ were derived from organic fertilizers (chicken manure, etc.), the different ranges may be related to varying residue levels in the manure covering the surface soil.

Spatial variograms are key instruments of geostatistical data analysis (Saito et al., 2005). The experimental FQ variograms assess spatial pattern differences between the five strata and are used in MSN pollutant estimation. Concerning NFX, the *r*-ratios for the five strata varied from 0.31 to 0.61. With the exception of strata 2, the ratios for the other strata were lower than the site (global) ratio, implying that the spatial FQ dependence was higher within strata than that at the site level. The spatial pattern of NFX concentrations between strata is also confirmed by the observed differences in variogram ranges. Spatial variability results for CFX and EFX were similar to that of NFX above. In sum, the geostatistics analysis of the data showed that stratification by plant type, indeed, reduced the FQ variance within strata.

3.3. Estimation of spatial FQ means

The means of the three FQ were estimated by various methods and the results are shown in Fig. 2a. The Box–Cox mean values are generally the smallest ones. The spatial CFX means calculated by the OK, stratified and MSN methods were between 104.4 and 107.3 μg/kg, i.e., they were very similar to each other (less than 2.9 μg/kg difference). The EFX means estimated by the same methods are between 16.7 and 18.6 μg/kg (less than 1.9 μg/kg difference). The corresponding NFX means varied between 55.7 and 58.5 μg/kg (less than 2.8 μg/kg difference).

The performances of the five estimation methods were compared in terms of the corresponding standard error of the mean estimates they generated, see plots in Fig. 2b. The results showed that the best pollutant estimation method was MSN, followed by OK and stratified random sampling. The arithmetic mean (AM) method produced estimates with the biggest estimation error. The estimation error of the CFX, EFX and NFX means were 5.0 μg/kg, 1.2 μg/kg and 3.9 μg/kg, respectively, which are equivalent to 42.3%, 40.0% and 69.9% of the estimation error associated with the AM estimates. This implies that the error of the MSN mean concentration estimate is reduced by 30.1–60.0%.

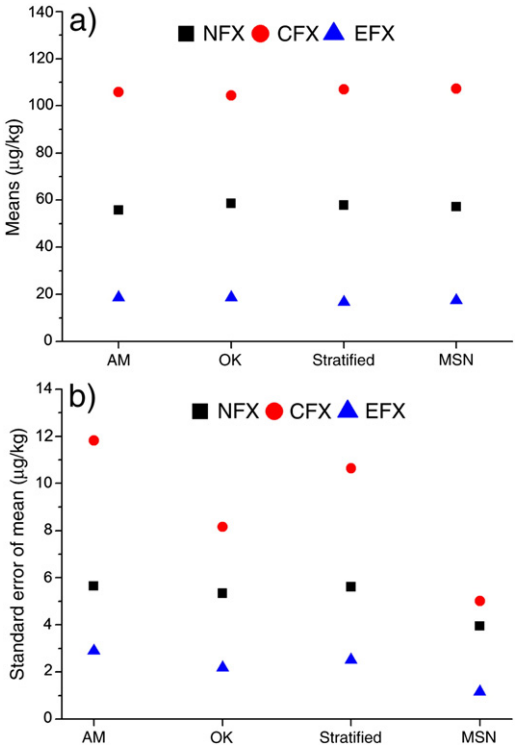

Fig. 2. (a) Means and (b) standard error of NFX, CFX and EFX concentrations estimated by various methods.

In sum, OK and stratified random sampling clearly outperformed the AM method. OK incorporates the spatial correlation of antibiotics to reduce the estimation error of the FQ means. Stratified random statistics takes spatially stratified non-homogeneity into account to improve the precision of the estimated FQ means. MSN combined the merits of the spatial stratification and OK methods to derive improved results compared to those obtained individually by the stratified random sampling and OK methods (Table 4).

3.4. Performance evaluation of the estimation methods using different sample sizes

The above results were further investigated using different sampling ratios. As already noted, the original set (consisting of 100 samples) was re-sampled randomly at the rates 30, 50 and 70% of the original sample number. Fig. 3 shows that as the sample size increases, the standard error deviation of the mean CFX estimates obtained by the four methods (AM, Stratified, OK and MSN) declines, and the precision of the mean estimates is improved accordingly. MSN produced CFX mean estimates with the smaller statistical error. Similar results were obtained for the EFX and NFX mean estimates (Figs. 4 and 5, respectively). The mean FQ estimates obtained by the four methods were ranked in order of decreasing estimation error, as follows: AM>Stratified>OK>MSN. The estimation errors of the four methods for the antibiotics decline at different rates as sampling rate increases. A possible reason is the different sensitivity of the four methods to the spatial heterogeneity features of these antibiotics. The relative error (standard error divided by mean) of mean FQ estimates obtained by the four methods declined, as the sample size increased from 30 to 100. If the maximum acceptable error of mean CFX estimate was set to 10%, the minimum sample size needed for Stratified, OK and MSN was 100,70,and 50 respectively. While more than 100 samples was needed for AM to obtain the acceptable relative error. The sample size required for mean CFX estimate by MSN can be reduced at least 30%. When the sample size was 100, the relative error of mean EFX estimate obtained by AM, Stratified and OK was

Table 4
Comparison of the four spatial statistic methods.

Methods	Spatial characteristics of the surface		BLUE[a]
	Auto-correlated	Non-homogenous	
Simple arithmetic	N	N	N
Stratification statistics	N	Y	N
Ordinary kriging	Y	N	Y[b]
MSN	Y	Y	Y

Note: Y/N means Yes/No.
[a] BLUE: best linear unbiased estimation.
[b] If the surface is homogeneous.

15.5%, 15.0% and 11.7%, respectively. Therefore, more samples were needed to reduce the relative error of mean EFX estimate. However, when the sample size was 50, the relative error of mean EFX estimate obtained by MSN was 8.2%. The sample size required for mean EFX estimate by MSN can by reduced at least 50%. For NFX, when the sample size is 100, the relative errors obtained by AM, Stratified and OK were 10.1%, 9.7%, 9.1%, respectively. When the sample size was 70, the estimate error of mean NFX obtained by MSN was 8.1%. The minimum sample size needed for Stratified, OK and MSN was 100, 100, and 70 respectively. More than 100 samples were needed for AM to obtain the acceptable relative error (less than 10%). The sample size required for mean NFX estimate by MSN can be reduced at least 30%.

The significance of antibiotic risks in surface soil is widely recognized. An accurate estimation of antibiotic residues in the soil is a prerequisite for ecological risk assessment and environmental health management. Accordingly, adequate pollutant estimation methods are sought that use assumptions that are consistent with the particular soil surface properties. The distribution of the antibiotic residues in soil exhibited considerable spatial heterogeneity features. Differences in antibiotic residues between strata were caused by various factors, including plant types, soil properties, cultivation conditions, and the sorption of antibiotics. The fertilizer amount used was different for the various vegetable species. Due to the varying physical and chemical characteristics of soil and the spatial variation of the environmental behavior (adsorption, degradation, leaching and plant accumulation) of the pollutants (Blackwell et al., 2009; Li et al., 2011; Sukul and

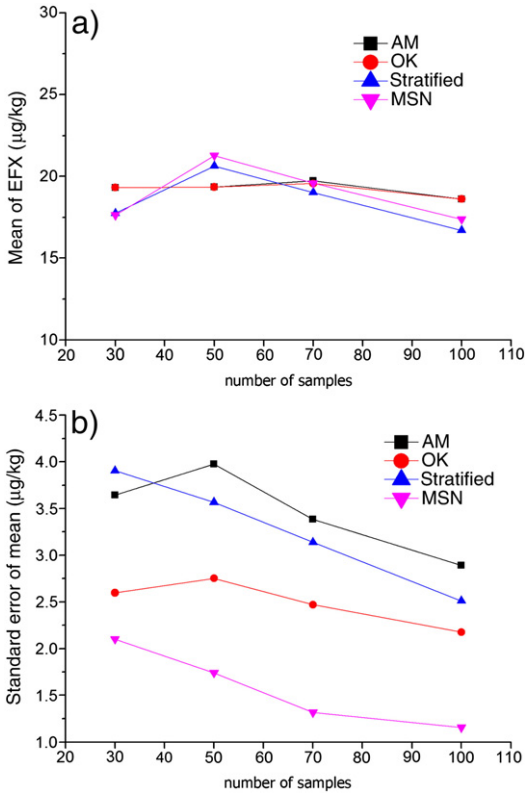

Fig. 4. Comparison of estimated EFX means and standard error of mean.

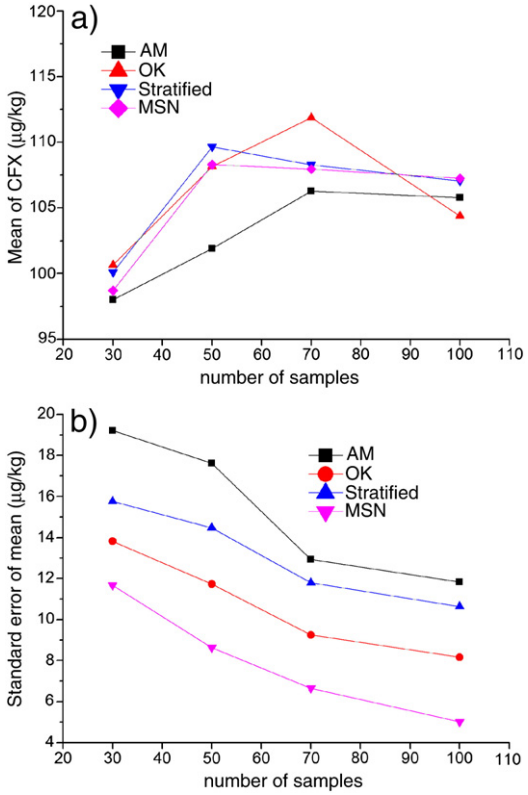

Fig. 3. Comparison of estimated CFX means and standard error of mean.

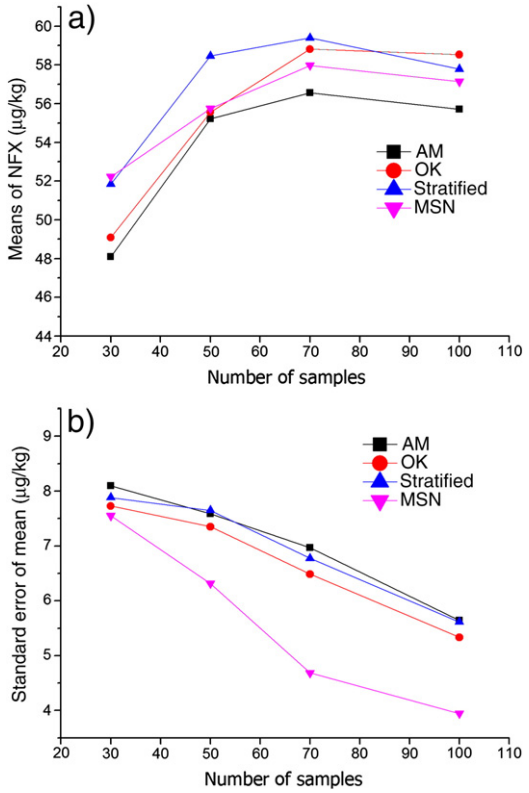

Fig. 5. Comparison of estimated NFX means and standard error of mean.

Spiteller, 2007), resulting in distinct antibiotic residue levels in soils with different plants and residue variances within the same strata. When the distribution of pollutant varied greatly at spatial, the traditional methods (AM, Stratified, OK) required more sample size to obtain an acceptable error of mean estimate. MSN can significantly reduce the sample size for mean FQ estimation. When investigating the antibiotic residues in soil at a large area (for example, a county or a city), the spatial pattern of antibiotic residues generally varies greatly, in which case the MSN technique can be used to reduce sample size and survey cost.

The results of the present study are of considerable public and economic importance. The focus of the study is the largest organic vegetable growing area in China, its production being sold to more than 200 cities nationwide. However, the antibiotic residues in soil frequently exceed the trigger value for soil (100 μg/kg) (Cengiz et al., 2010). The environmental risk of antibiotic residues must be further assessed when the exposure concentration is higher than the trigger value (Montforts et al., 1999). Fluoroquinolone antibiotics in soil can have ecotoxicological impacts on photosynthetic organisms and accumulate in the vegetables (Aristilde et al., 2010). The main source of antibiotics residue in soil is manure fertilization. To prevent deterioration of soil quality and protect food safety, fertilization must be properly managed and controlled. The concentration of antibiotics residue in manure should be sterilized to an acceptable level before applied to vegetable land, among other things.

4. Conclusions

The simple AM estimates of the CFX, EFX and NFX mean concentrations in surface soil were 105.8 μg/kg, 18.6 μg/kg and 55.7 μg/kg, respectively. The estimated means and error variances of the three antibiotics changed within soil sub-regions stratified by plant type. The CFX, EFX and NFX means estimated by the MSN method were 107.3 μg/kg, 17.4 μg/kg and 57.1 μg/kg, respectively. The corresponding standard error deviation of the mean estimates were 5.0 μg/kg, 1.2 μg/kg and 3.9 μg/kg, respectively. Compared to the AM estimate, the error deviation of the MSN mean estimate was accordingly reduced by 30.1 to 60.0%. When the sample size varied from 30 to 100, MSN was always the best FQ estimator across space; it performed much better than the other methods when the sample size was small and the surface was non-homogeneous stratified (this condition commonly exists in practice and is caused by the variation of plant types, cultivation condition, soil properties, etc.). In region investigation of antibiotic residues in soil, MSN can significantly reduce the sample size.

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