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ORIGINAL ARTICLE

Spatial variability of soil available Zn and Cu in paddy rice fields of China

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Abstract As a source of nutrient supplements, the deficiency or excess of micronutrients in soil is directly connected to the plant uptake and, thereby, status of micronutrients in the human population. Proper management of micronutrients requires an understanding of the variations of soil micronutrients across the fields. This study is to investigate the spatial patterns of soil available Zn and Cu in paddy rice fields. Four hundred and sixty three soil samples were taken in Hangzhou–Jiaxing–Huzhou (HJH) watershed in Zhejiang Province, China, and available Zn and Cu were analyzed using an atomic adsorption spectrometer. Geostatistical semivariograms analysis indicated that the available Zn and Cu were best fitted to a spherical model with a range of 40.5 and 210.4 km, respectively. There were moderate spatial dependences for Zn and Cu over a long distance and the dependence were attributed to soil types and anthropogenic activities. The overlay analysis of spatial patterns and soil types gave us greater understanding about how intrinsic factors affect the spatial variation of available micronutrients. Based on the above, macroscopically regionalized management of soil available micronutrients and the implications to potential risk were discussed.

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Introduction

Proper management of soil nutrients is important for meeting the needs of ever-increasing population of the world without deteriorating the environment. Surveys and maps illustrating the geographic distribution of soil micronutrient availability would provide guidance for proper management of nutrients in soils, and are necessary for a better understanding of the nature and extent of micronutrient deficiencies and toxicities in plants, livestock and humans (Jeffrey and Robert 1999). Hangzhou–Jiaxing–Huzhou (HJH) watershed in Zhejiang Province, China, is the key rice production area. With the rapid development of agriculture in Zhejiang Province, the management of soil nutrients in the HJH watershed is directly connected with the crop yield and agricultural non-point source pollution. Spatial variability of nutrients is thought to be one of the key factors to consider for precision agricultural management.

The spatial variability of soil micronutrients may be affected by soil parent materials and anthropogenic sources. Normal agricultural practices generally cause enrichment of Zn and Cu elements (Kashem and Singh 2001; Mantovi et al. 2003). In agricultural ecosystems where animal farming and related agricultural practices are intensive, heavy metals can reach the soil due to application of liquid and soil manure. These practices are an important source of heavy metals, particularly Cu (Nicholson et al. 2003; Jose et al. 2006).

In recent years, geostatistics has been proven to effectively assess the variability of soil nutrients (Webster and Oliver 2001; Corwin et al. 2003; Mueller et al. 2003). Geostatistical methods have been applied to analyze soil variability from a spatial resolution of centimeters to a few meters (Webster and Nortcliff 1984; Cahn et al. 1994; Solie et al. 1999; Wilcke 2000) and then to a regional scale (Yost et al. 1982; Chien 1997; White et al. 1997; Liu et al. 2004).

Primary objectives of this research were: to examine the spatial dependence of soil available micronutrients (Zn and Cu) in paddy rice fields in relation to soil types, to determine the controlling factors for the spatial variability, and to generate large-scale distribution patterns of significant metal sources to facilitate estimates at unsampled locations. These aspects have not previously been studied at this level in the HJH watershed and the study could provide insight for agronomic management and environmental evaluations.

Materials and methods

Study area

The HJH watershed, located in the northern part of Zhejiang Province, China, was selected in this study. The region includes the counties of Jiaxing, Jiashan, Tongxiang, Haining, Haiyan, Pinghu, Huzhou city, Deqing, Anji, Changxing, a large part of Hangzhou city, and a part of Lin'an County (Fig. 1). Dense drainage ditches are distributed in the watershed, forming a network of waterways. The HJH watershed covers 6,390.8 km^2, and is one of the primary food production regions in Zhejiang Province with dominant paddy soil and rice (*Oryza satiya*) crop.

Fig. 1 Location of the study area

Soil sampling and data analysis

Considering the uniformity of soil sample distributions and soil types in the study area, we sampled 460 soil samples from different locations in paddy fields in 2001 at an interval of 5 km. Distribution of sampling points is presented in Fig. 2. All soil samples were taken at a depth of 0–15 cm and air-dried with stones and coarse plant roots or residues removed. Samples were thoroughly mixed and ground to pass a 0.149-mm sieve, then stored in plastic bags prior to chemical analysis. The pH values of the soils ranged from 4.14 to 8.26 with a mean of 5.81. Available Zn and Cu were extracted with diethylenetriaminepentaacetic acid (DTPA). Zn and Cu concentrations in the extracts were determined by flame atomic absorption spectrometry (AAC) (Sharma et al. 2004; Lindsay et al. 1978).

Geostatistical analysis and simple statistical analysis

Geostatistical method

Geostatistics was used to estimate and map soils in unsampled areas (Goovaerts 1999). Among the geostatistical techniques, Kriging is a linear interpolation procedure that provides a best linear unbiased estimation for quantities, which vary in space. Kriging estimates are calculated as weighted sums of the adjacent sampled concentrations. That is, if data appear to be highly continuous in space, the points closer to those estimated receive higher weights than those farther away (Cressie 1990).

Semivariograms were developed in this study to evaluate the degree of spatial continuity of soil available micronutrients among data points and to establish a range of spatial dependence for each soil available micronutrient using a lag distance of 1,000 m and lag tolerance of 500 m. Information generated through variogram was used to calculate sample weighted factors for spatial interpolation by a Kriging procedure (Isaaks and Srivastava 1989).

Semivariance, $\gamma(h)$, is computed as half the average squared difference between the components of data pairs (Wang 1999; Goovaerts 1999)

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [Z(x_i) - Z(x_i + h)]^2 \quad (1)$$

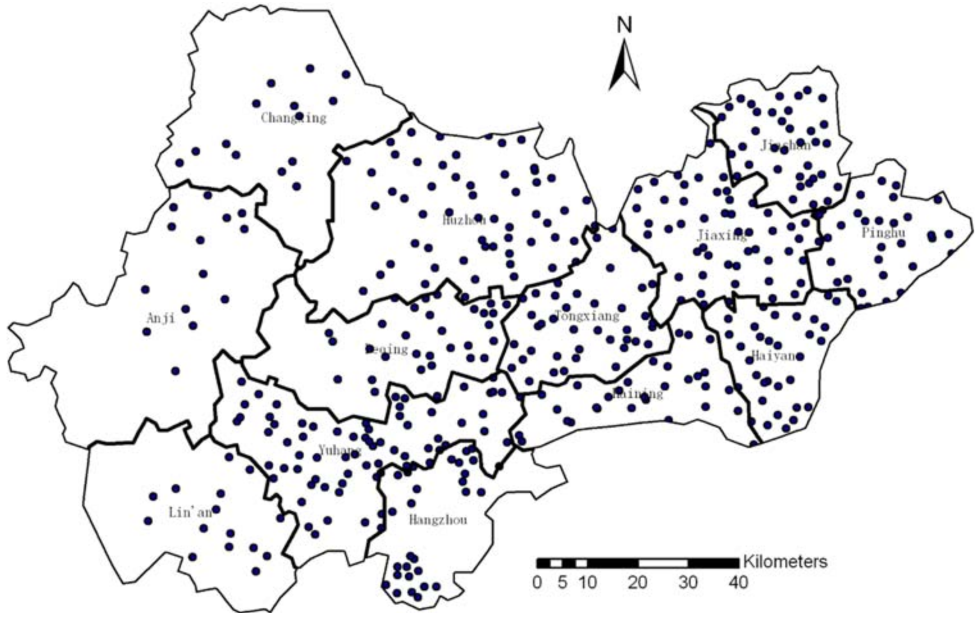

Fig. 2 Distribution of sampling points

where *N(h)* is the total number of data pairs separated by a distance h, Z represents the measured value for soil property, and x is the position of soil samples.

Several standard models are available to fit the experimental semivariogram, e.g., spherical, exponential, Gaussian, linear and power models (Wang 1999). In this study, the fitted spherical model was used.

The spherical function is:

$$\begin{aligned} \gamma(h) &= C_0 + C\left[\frac{3}{2}\frac{h}{a} - \frac{1}{2}\left(\frac{h}{a}\right)^3\right] \quad 0 < h \le a \\ \gamma(h) &= C_0 + C \qquad\qquad h > a \end{aligned} \tag{2}$$

where C_0 is the nugget variance (h = 0), C is the structural variance and a is the spatial range.

Nugget variance represents the experimental error and field variation within the minimum sampling spacing. The nugget/sill ratio can be regarded as a criterion to classify the spatial dependence of soil properties. If the ratio is less than 25%, the variable has strong spatial dependence; between 25 and 75%, the variable has moderate spatial dependence; and greater than 75%, the variable shows only weak spatial dependence (Cambardella et al. 1994; Chang et al. 1998; Chien et al. 1997).

Simple statistical analysis

Kolmogrov–Smirnov (K-S) test for goodness-of-fit was performed to test whether the datasets for soil available micronutrients were normally distributed (Sokal and Rohlf 1981). It is shown in Table 1 that the datasets for available Cu were normally distributed while Zn concentrations were not normally distributed. Therefore, further analysis of Zn was based on their logarithmically transformed values of Zn concentration. Correlation analysis among the soil available micronutrients and soil grain size, pH, organic matter (OM) and CEC was performed in SPSS 12.0 in this study.

Stepwise regression analysis was also used to select the main factors affecting soil available Zn and Cu, with SPSS 12.0 employed. Often there will be many possible explanatory variables in the data set and, by using a stepwise regression process, the explanatory variables can be considered one at a time. The one that explains most variation in the dependent variable will be added to the model at each step. The process will stop when the addition of an extra variable will make no significant improvement in the amount of variation explained. The regression equation is:

$$Y = b_0 + b_1X_1 + b_2X_2 + \cdots + b_nX_n$$

where Y represents the dependent variable and X is the independent variable. The values b_0, b_1, b_2, …b_n are called the regression coefficients and are estimated from the collected data by a mathematical process called least squares, explained by Altman (1991).

Results and discussion

Statistical characterization of data

Descriptive statistics

Table 1 presents the summary statistics of the datasets for soil properties including the two available micronutrients. The mean value of available Zn (1.97 mg kg^{-1}) in 2001 is

Table 1 The statistical values of soil properties in the HJH watershed

Soil properties	Sample size	Mean	Minimum	Maximum	S.D.	Kurtosis	Skewness	CV/ %
Clay (<0.002 mm)/%	460	14.28	4.92	23.5	2.85	0.82	0.13	19.99
Slit (0.05–0.002 mm)/%	460	69.09	36.4	80.2	6.94	3.08	−1.55	10.06
Sand (2–0.05 mm)/%	460	16.64	5.13	51.4	7.55	3.94	1.75	45.4
pH	460	5.81	4.14	8.26	0.68	1.41	1.09	11.68
Organic matter (OM)/g kg^{-1}	460	33.95	10.92	61.4	9.06	−0.07	−0.22	26.69
CEC/$cmol^{+}$ kg^{-1}	460	14.82	4.20	24.8	3.88	−0.54	−0.21	26.23
Available Zn/mg kg^{-1}	460	1.97	0.5	7.1	1.21	6.66	2.28	61.25
Logarithm of available Zn	460	0.23	−0.3	0.85	0.22	0.29	0.47	94.31
Available Cu/mg kg^{-1}	460	4.8	0.7	9.63	1.72	0.07	0.33	35.87

S.D.: standard deviation; *C.V.*: coefficient of variation

higher than that (1.45 mg kg^{-1}) in 1982 when the general second soil survey was performed. The mean available Cu (4.8 mg kg^{-1}) also increased when compared to the mean value of 3.28 mg kg^{-1} in 1982. The coefficients of variation of available Zn and Cu in 2001 were 61.25 and 35.87%, respectively, suggesting that available Zn had greater variation among the soils than available Cu.

Correlation analysis

To understand the effect of soil property on available micronutrients, the correlation between available micronutrients and soil properties (grain size, pH, organic matter, cation exchange capacity) was analyzed (Table 2). The result showed that soil available Zn was correlated with Cu significantly ($P < 0.01$). Available Zn was positively correlated with sand and organic matter ($P < 0.05$), and negatively correlated with silt ($P < 0.01$). Available Cu was significantly positively correlated with clay, silt, OM and cation exchange capacity (CEC; $P < 0.01$). The correlation coefficient r between Cu and CEC was the highest among all soil properties with a value of 0.5035. In addition, Cu has a negative correlation with sand and pH.

Table 2 The correlation between available micronutrients and soil properties

	Available Zn	Available Cu
Available Zn	1	
Available Cu	0.1677**	1
Clay (<0.002 mm)	−0.0023	0.1627**
Slit (0.05–0.002 mm)	−0.1302**	0.1457**
Sand (2–0.05 mm)	0.1211*	−0.1943**
pH	−0.0602	−0.1172*
Organic matter (OM)	0.1163*	0.1767**
CEC	−0.0084	0.5035**

* $P < 0.05$;** $P < 0.01$

Stepwise regression analysis

For available Zn and Cu, soil grain size, pH, OM and CEC were selected as independent variables to perform the stepwise regression analysis. The result represented in Equation 3 indicated that the available Zn was mainly related to soil silt and OM, and available Cu were mainly affected by CEC and pH.

$$\begin{aligned} Y_{Zn} &= 3.428 - 0.029X_{Silt} + 0.019X_{OM} \\ Y_{Cu} &= 3.947 + 0.253X_{CEC} - 0.487X_{pH} \end{aligned} \quad (3)$$

Semivariogram analysis

Figure 3 presents the semivariogram and fitted model for available Zn and Cu. The attributes of the semivariograms

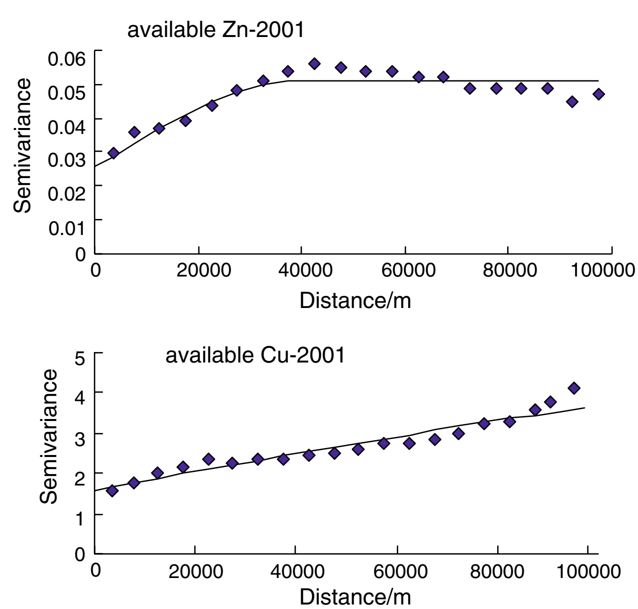

Fig. 3 The Semivariogram for soil available micronutrients in the HJH watershed in 2001

for each soil available micronutrient are summarized in Table 3.

Semivariogram results showed that the two soil available micronutrients were best fit with a spherical model. The nugget/sill ratios for available Zn and Cu were 49.9 and 33.4%, respectively, suggesting moderate spatial dependence at the large scale of the HJH watershed.

The spatial variability of soil properties may be affected by intrinsic (soil formation factors, such as soil parent materials) and extrinsic factors (soil management practices, such as fertilization). Usually, strong spatial dependence of soil properties can be attributed to intrinsic factors, and weak spatial dependence can be attributed to extrinsic factors (Cambardella et al. 1994). The result in Table 3 showed that the extrinsic factors such as fertilization, cultivation and other soil management practices weakened the spatial correlation after a long history of cultivation. The nugget/sill ratio of soil available Cu was lower than that of Zn, indicating soil available Cu had stronger spatial correlation than available Zn. This result was consistent with the result that the CV value of available Zn was higher than that of Cu (Table 1). The range of available Cu was 210.4 km, much larger than that of available Zn. The stronger spatial variability and smaller range suggest that smaller sampling intervals are needed for Zn than for Cu.

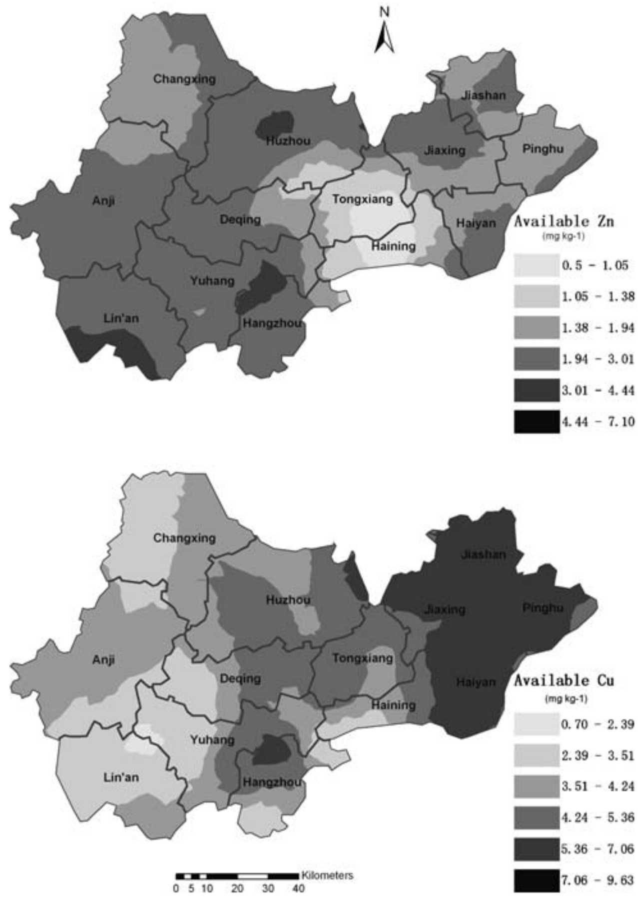

Fig. 4 The filled contours maps of soil available micronutrients in 2001 in the HJH watershed

Spatial distributions and overlay analysis

Figure 4 shows the spatial patterns of the two soil available micronutrients generated from Kriging analysis based on their semivariograms parameters (Table 4). There is a strong spatial variability in soil micronutrients such as Zn and Cu due to the variation in the parent materials. In addition, crop species and cultivars vary widely in their ability to mobilize and assimilate micronutrients in the rhizosphere (Jeffrey and Robert 1999). Therefore, large spatial variations of available Zn and Cu over long distances are expected.

In order to understand how intrinsic factors affect the spatial variation of available Zn and Cu, the soil map of the HJH watershed was intersected with the filled contours maps of soil available micronutrients. The overlay analysis suggested a strong correlation between soil type and available micronutrients.

The areas of soil available Zn with 0.5–1.0 mg kg^{-1} concentration accounted for 8.9% of the entire HJH watershed. This 8.9% area is mostly dominated by paddy soil (81.98%) and coastal Solonchaks (10.43%). For soil available Zn content in the range of 1.0–3.0 mg kg^{-1}, the area covered 88.14% of the HJH watershed with paddy soil (50.9%) and red soil (28.3%) types. A small proportion of fluvo-aquic soils, coastal solonchaks, skeletal soils and yellow earths were also interspersed. The high Zn concentration (> 3 mg kg^{-1}) area only accounted for 2.96% of the total study area, of which red soils covering 56.7%, paddy soils 25.4%, and limestone soils 15.1%.

The areas of soil available Cu between 0.7 and 2.39 mg kg^{-1} accounted for 0.61% of the study area with the primary soil type as red soil. Eighty three percent of the HJH watershed has available Cu concentration in the range

Table 3 The best-fitted semivariogram models and their parameters for soil available micronutrients in the HJH watershed

Soil properties	Model	C_0 Nugget	$C + C_0$ Sill	$C_0/C + C_0$ nugget/sill	Range/km	R^2
Available Zn	Spherical	0.026	0.051	0.499	40.5	0.844
Available Cu	Spherical	1.59	4.765	0.334	210.4	0.926

Table 4 The quantity of different livestock in the HJH watershed in 2001

County	Pig	Poultry	Cattle	Sheep	Total	Pig density
Hangzhou	889,500	10,614,100	9,085	21,700	11,534,400	289.93
Yuhang	502,100	13,652,700	1,857	162,600	14,319,300	410.88
Jiaxing	2,112,300	9,928,800	469	207,400	12,249,000	539.54
Haining	603,400	5,548,200	0	401,700	6,553,300	903.29
Pinghu	1,052,800	2,084,200	90	28,900	3,166,000	1960.52
Jiashan	1,028,200	6,908,100	134	12,300	7,948,700	2028.01
Haiyan	1,106,200	2,123,100	0	140,800	3,370,100	2177.56
Tongxiang	555,200	11,341,700	0	602,300	12,499,200	763.69
Huzhou	742,700	8,152,200	316	387,900	9,283,100	127.68
Deqing	393,100	4,309,100	266	6,900	4,771,500	419.98
Changxing	365,900	5,878,400	1,836	154,400	6,400,500	255.87

of 2.39–5.36 mg kg^{-1}, of which 44.5% paddy soils and 31.38% red soils. The areas with high Cu concentration (5.36–7.06 mg kg^{-1}) were found to be 16.37 percent of the HJH watershed, with paddy soil accounting for 97.2% of the area.

The spatial distribution soil available Cu showed distinct geographic trends. Most of the study area exhibited low Cu concentrations. The areas of high Cu concentrations were mainly distributed in Jiashan, Jiaxing, Pinghu and Haiyan (Fig. 4). Cu concentrations were especially high in Jiashan and parts of Jiaxing and Haiyan, mainly due to the excessive livestock manure fertilization. The livestock industry has become an important component of the rapidly developing Chinese rural economy. Meanwhile, the livestock manure, such as pig slurries with high Cu concentration, was mainly used as a fertilizer for the arable soil, which further contributed to the available Cu content in the soil (Huang 2002). The statistics of livestock breeding in the HJH watershed in 2000 are listed in Table 4 and are based on the Zhejiang Statistical Yearbook (2001). Compared to 1990, the numbers of pigs increased by 3,137,600 whose manure use as fertilizer could contribute to the elevated Cu in soils (Qian 2001). In 2001, Jiaxing County contained the largest number of pigs followed by Haiyan, Pinghu and Jiashan. This area is characterized by high-density animal husbandry and intensive utilization of manure as fertilizers. This practice is so widespread that it is easy to hypothesize that the major source for Cu in the soil is manure application. In order to test this hypothesis, the correlation between the density of pig distribution and the mean values of available Cu concentration in various counties were analyzed, and the high determination coefficient ($R^2 = 0.58$) further proved the contribution of livestock manure in the HJH watershed to high Cu concentration. Mantovi et al. (2003) also showed a comparison between the metal contents of liquid manure and normal heavy metal concentrations in soils. They also demonstrated that the Cu content in pig slurries is 10–40 times higher than in soil.

Soil micronutrient classification for the Zhejiang province is displayed in Table 5. It is seen from Fig. 4 that the soil available Zn in the HJH watershed is at the high and middle levels, and there are almost no areas where the Zn content is below 0.5 mg kg^{-1}. Therefore, we could divide the entire study area into two regionalized sections: Section I (>1.0 mg kg^{-1}) and Section II (0.50–1.0 mg kg^{-1}). Section I included the major part of the HJH watershed where the soil available Zn reached high levels. Section II mainly included Changxing, Tongxiang and Haining where medium levels of soil Zn were distributed.

The available Cu in the HJH watershed can also be regionally managed. The available Cu can be separated into two parts: Section I (0.7–5.13 mg kg^{-1}) and Section II (5.13–9.63 mg kg^{-1}). Section I contained the western portion of the HJH watershed, which includes Changxing, Anji, Lin'an, Huzhou, Deqing, Yuhang, Hangzhou, Tongxiang and Haining. Section II contained the eastern portion of the HJH watershed, which includes Jiashan, Jiaxing, Pinghu and Haiyan. These areas showed high levels of the available Cu with concentrations between 5.13 and 9.63 mg kg^{-1}. The regionalization of soil available micronutrients could provide insight for further agronomic management of the region, such as the precision fertilization.

Table 5 Classification criterions for soil micronutrients in Zhejiang Province

Available micronutrients	High		Middle	Low	
	1	2	3	4	5
Zn/mg kg^{-1}	>3	1–3	0.5–1	0.3–0.5	≤0.3
Cu/mg kg^{-1}	>2	1.0–2.0	0.2–1.0	0.1–0.2	≤0.1

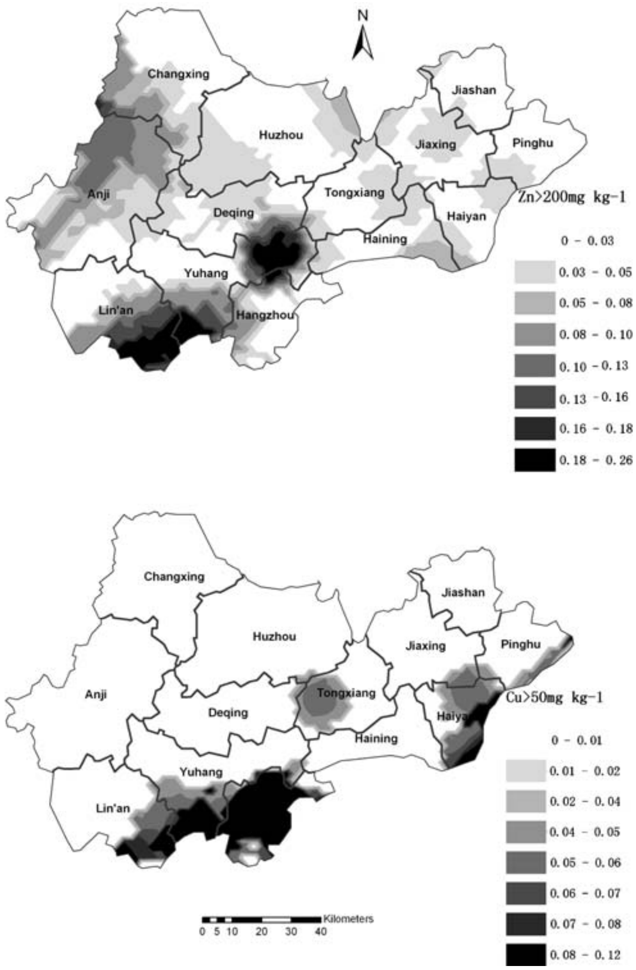

Fig. 5 The estimated probability maps of total Zn and Cu

In our previous research (Liu et al 2006), the estimated probability of excessive total Zn and Cu was delineated based on the guide values issued by the Chinese Environmental Quality Standard for Soils (GB 15618–1995) (State Environmental Protection Administration of China 1995) (Fig. 5). The probability map of Zn exceeding the guide value of 200 mg kg^{-1} highlighted many areas of high risk. In particular, the highest risk areas are distributed in Yuhang and Lin'an. For soil Cu, the areas with high risk are mainly located in South Yuhang, East Hangzhou and Haiyan. In the near future, the high risk of total Zn and Cu pollution will have repercussions on the available amount of Zn and Cu, and, consequently, the environmental quality of this area. Moreover, soil can also affect human health in several ways leading either to specific diseases or to more general ill health. Most examples of ill health associated with the soil are caused by concentrations of elements including Zn and Cu in food or water that are either deficient or toxic (Oliver 1997). Greater understanding will require multidisciplinary investigation for the complex relations between soil and human health. Therefore, this study can give some information for soil pollution assessment and human health.

Conclusions

This study showed the spatial variability of soil available micronutrients in paddy rice fields. Over a long history of various land management, the spatial variability of available Zn and Cu was caused not only by the soil parent materials but also by anthropogenic activity. The high available Cu concentrations in the HJH watershed were due to the high density of animal farming and intensive utilization of manure as fertilizers. Based on the provincial classification standard of soil micronutrients, regionalized management of available Zn and Cu was recommended. Due to the difficulty in developing the guide values for soil heavy metal availability, total amounts of Zn and Cu were employed to give an indication of the potential risk of available Zn and Cu. Moreover, these results could provide insight for the potential of agronomic measure adjustments, such as fertilization, and the environmental risk assessment.

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