



## Variability of copper availability in paddy fields in relation to selected soil properties in southeast China

Chunfa Wu<sup>a,b,\*</sup>, Yongming Luo<sup>a,\*</sup>, Limin Zhang<sup>c</sup>

<sup>a</sup> Key Laboratory of Soil Environment and Pollution Remediation, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China

<sup>b</sup> Yantai Institute of Coastal Zone Research for Sustainable Development, Chinese Academy of Sciences, Yantai 264003, China

<sup>c</sup> Agricultural Extension Service, 314400 Haining, China

### ARTICLE INFO

#### Article history:

Received 22 June 2009

Received in revised form 9 January 2010

Accepted 15 February 2010

Available online 11 March 2010

#### Keywords:

Copper availability

Geostatistics

Spatial variability

Soil property

Correlation

### ABSTRACT

Copper (Cu) is an essential nutrient element for plant growth and is a toxic heavy metal in excess concentrations. As such, its concentration and availability in soils are of great agricultural and environmental concern. Availability and spatial pattern of copper in relation to selected soil properties in surface soils were evaluated for an agricultural region in southeastern China. A total of 224 topsoil samples (0–15 cm) were collected from paddy fields in a study area of 731 km<sup>2</sup>. We measured total Cu and DTPA-extractable Cu (available Cu) concentrations, soil pH, soil organic matter content (SOM), total nitrogen, available phosphorus, available potassium, and cation exchange capacity (CEC). We estimated Cu availability by calculating the ratio of available Cu to total Cu concentration. The results of our chemical analyses indicated that both total Cu and available Cu concentrations had a wide range throughout the study area. In addition, we measured slight Cu accumulation in paddy fields of the study area in comparison to background levels at Zhejiang Province scale. Correlation analysis revealed that available Cu concentration was positively correlated with total Cu concentration, CEC and SOM as indicated by moderate to high correlation coefficients ( $r = 0.64\text{--}0.82$ ), and Cu availability was directly correlated with SOM, pH and Cu concentration with moderate to high positive correlation ( $r = 0.47\text{--}0.82$ ) at 0.01 level of significance. Spatial distribution maps illustrated that total Cu concentration and available Cu concentration had similar distribution trends with the highest concentrations in the northeast region and low concentrations in the southwest region of the study area. Copper availability ratio had a spatial distribution trend with high ratios in the northeast region and low ratios in the central region of the study area. Soil properties influencing the spatial distribution of Cu availability were SOM and pH, in addition to the concentration of available Cu.

© 2010 Elsevier B.V. All rights reserved.

### 1. Introduction

Copper (Cu) is not only an essential nutrient for plant growth (Alloway, 1995) but also a poisonous heavy metal element that is potentially hazardous in the environment (Moreno et al., 1997). Copper is involved in photosynthesis and respiration as an important component of various enzymes (Demirevska-Kepova et al., 2004). Copper deficiency is known to cause grain sterility in many cereal crops (Mizuno and Kamada, 1982) and severe depression of crop yields (Qin et al., 1992). Higher than normal Cu supply, however, usually inhibits root growth more than shoot growth (Lexmond and

van der Vorm, 1981), and causes plant toxicity (Tisdal et al., 1993). The contamination of the food chain by Cu is detrimental to human and animal health. Therefore, soil Cu concentration and availability are of agricultural and environmental significance.

Sources of soil Cu include soil parent material; mining and smelting residues; urban, industrial and agricultural wastes; and agrochemicals. Accepted agricultural practices can add Cu to soils through application of liquid and solid manure or inorganic fertilizers (Prasad et al., 1984; Mantovi et al., 2003; Pietrzak and McPhail, 2004). Increased urbanization, including industrial and mining activities, also has added Cu to soils (Boojar and Goodarzi, 2007). Due to its high affinity for organic matter, Cu is not readily leached from the soil profile and tends to accumulate in surface soils (McBride et al., 1997). Continuing accumulation of Cu in surface soils, particularly in agricultural lands, will increase the risk of phytotoxicity, and eventually threaten food safety and security.

Cu in soils generally exists in several forms, including free ions in the soil solution: exchangeable, organic, precipitated, and residual (Shuman, 1985). Most Cu in soils exists in unavailable forms with only low concentration of Cu existing in available forms (Shuman, 1991) with the proportion of available and unavailable forms varying widely among

*Abbreviations:* Cu, copper; TN, total nitrogen; SOM, soil organic matter; AP, available phosphorus; AK, available potassium; CEC, cation exchange capacity; GPS, global position system; DTPA, diethylenetriamine penta-acetic acid; EDTA, ethylenediaminetetraacetic acid; CVs, coefficients of variation;  $r$ , correlation coefficient;  $P$ , the significance probability of  $t$  test.

\* Corresponding authors. Key Laboratory of Soil Environment and Pollution Remediation, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China. C. Wu is to be contacted at Tel.: +86 025 86881012. Luo, Tel.: +86 025 86881101.

E-mail addresses: [wchf1680@sina.com](mailto:wchf1680@sina.com) (C. Wu), [ymluo@issas.ac.cn](mailto:ymluo@issas.ac.cn) (Y. Luo).

soils within and between agro-ecological regions (Jeffrey and Robert, 1999). The chemical forms of metals in soil can vary strongly depending on soil properties (Lee and Kao, 2004). Many studies have shown that soil properties such as pH, soil organic matter content (SOM), cation exchange capacity (CEC), and soil texture, influence soil Cu concentration (Kabata-Pendias and Pendias, 2001; Sterckeman et al., 2004; Micó et al., 2006). In addition, soil microenvironments also influence the availability of soil Cu (Jenne, 1968; Shuman, 1988). The total concentration of metals is, in general, considered in soil contamination assessment studies (Kabata-Pendias and Pendias, 2001; Amini et al., 2005), and pollution source identification (He et al., 1997; Jung, 2001). Several studies indicate that the available concentration of soil metals is better than total concentration for the prediction of metal transfer from soil to crops and for environmental hazard assessments (Brun et al., 1998; Wang et al., 2006). It is important to study Cu availability and its controlling factors in agricultural soils in order to modify Cu availability and prevent excessive Cu from entering the food chain. By modifying environmental factors controlling Cu accumulation or pollution, risks to soil, plant and human health can be reduced.

Proper management of soil nutrients is important for meeting the needs of an ever-increasing population of the world without deteriorating the environment and harming human health. Characterizing total and available Cu concentration, including the ratio of available Cu concentration to total Cu concentration in agricultural soils and fertilizers is necessary to protect the soil environment. Available Cu concentration and Cu availability ratio are two important measures of Cu status in soil systems. Soil surveys and maps illustrating the geographic distribution of soil micronutrient availability would provide improved guidance for proper management of nutrients in soils. Such resource inventory data 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). Such inventories require the accurate delineation of the spatial distribution of soil Cu availability based on a limited number of samples in agricultural and environmental landscapes.

In the past decades, many studies on Cu have been conducted. However, most of these studies have focused on the total content of heavy metals or on their toxicity (Ma and Rao, 1997). Few investigations have been conducted with respect to characterizing the variability of Cu availability in relation to selected soil properties in agricultural soils. The objectives of this study were to: (1) assess the status of Cu accumulation and Cu pollution; (2) analyze the relationship between soil properties on Cu availability; and (3) characterize the spatial variability of Cu availability in paddy fields of Haining County, China.

## 2. Methods and materials

### 2.1. Description of study area

This study was conducted in an agricultural region of Haining County in southeast China. The study area is located in the Hang-Jia-Hu Plain, northeastern region of Zhejiang Province, China (Fig. 1). The study area is bounded by longitude 120°18'–120°52' East and latitude 30°15'–30°35' North, encompassing an area of 731 km<sup>2</sup>. The study area is in the northern subtropical zone of monsoonal climate with a temperate and humid climate throughout the year with four distinct seasons. The average annual temperature is 15.9 °C and the mean annual precipitation is approximately 1190 mm. Paddy field is the dominant land use/land cover of arable land, and paddy soil (Gleysols) is one of the many kinds of anthropogenic and natural soils found in the study area. In this area, the soils in a majority of study area are formed from recent estuarine alluvia and the soils in the southern region are formed from ancient estuarine alluvia. Soil texture has a distribution trend in which high sand content occurs in southern region and high clay content occurs in the northern region.

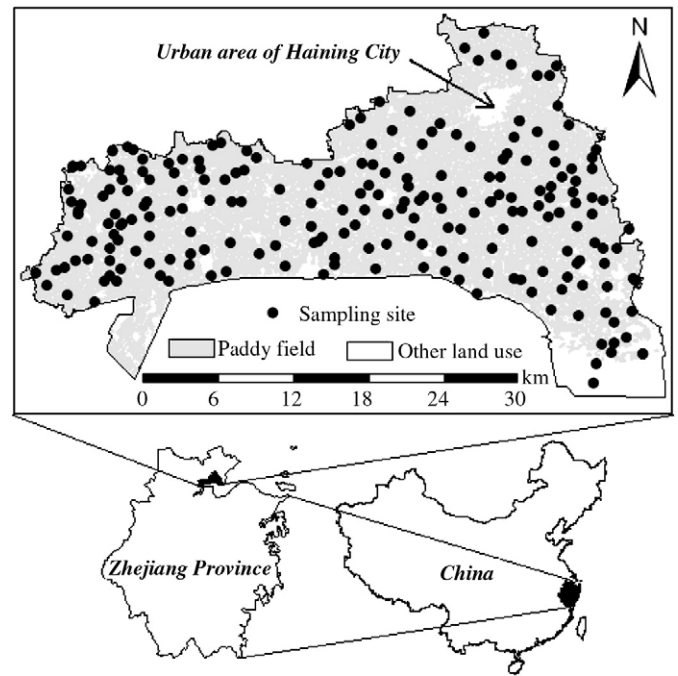


Fig. 1. The location of study area and distribution of sampling sites.

The area is dominated by agricultural production in one of the most developed regions south of the Yangtze River in Zhejiang Province. The history of this primary food production zone spans approximately 3000–4000 years (Shi et al., 2008).

### 2.2. Sampling design and soil analysis

A total of 224 topsoil samples (0–15 cm) were collected from paddy fields in November 2005 with consideration of land use uniformity, soil type, and a uniform distribution of samples to ensure samples were located in paddy fields and were collected from each type of paddy soil (Fig. 1). The soil type was classified according to the Chinese Soil Taxonomic Classification (Zhang and Gong, 2004). When sampling, soils in top layer (0–15 cm) of 6–8 points in each site of an area of approximately 0.1–0.2 ha were collected then fully mixed, divided into parts of 1–2 kg each, then delivered to the laboratory for analysis. The locations of all sample sites were recorded using a handheld global position system (GPS). All samples were air-dried at room temperature (20–22 °C), stones or other debris were removed, and then sieved to achieve a 2 mm particle size fraction. Portions of each sample (approximately 100 g) were ground in an agate grinder and sieved through 0.149 mm mesh. The prepared soil samples were then stored in polyethylene bottles for analysis.

Soil pH was measured by pH meter (Sartorius Basic pH meter PB-10) with a soil/water ratio of 1:2.5. Eighty representative soil samples from paddy fields were selected randomly by land use and soil type. The CEC was determined using a 1.0 mol L<sup>-1</sup> ammonium acetate solution. Soil organic matter (SOM) was determined by wet oxidation at 180 °C with a mixture of potassium dichromate and sulfuric acid (Agricultural Chemistry Committee of China, 1983). Total nitrogen (TN) was determined by Kjeldahl method with H<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O<sub>2</sub> digestion. Available phosphorus (AP) was extracted using 0.03 mol L<sup>-1</sup> NH<sub>4</sub>F–0.025 mol L<sup>-1</sup> HCl or 0.5 mol L<sup>-1</sup> NaHCO<sub>3</sub> (based on pH values), and analyzed using the molybdenum-blue method. Available potassium (AK) was extracted using 1 mol L<sup>-1</sup> NH<sub>4</sub>OAc and then measured by flame emission spectrometry (Kim, 2005). Total Cu concentration was measured by inductively coupled plasma mass spectrometry (ICP-MS) after soil samples were digested

**Table 1**  
Summary statistics<sup>a</sup> for Cu concentrations and six soil properties<sup>b</sup> in paddy fields.

	T-Cu mg kg <sup>-1</sup>	A-Cu mg kg <sup>-1</sup>	SOM g kg <sup>-1</sup>	pH	CEC cmol(+) kg <sup>-1</sup>	TN g kg <sup>-1</sup>	AP mg kg <sup>-1</sup>	AK mg kg <sup>-1</sup>	Available ratio %
Min	15.3	1.46	5.7	4.40	7.27	0.45	1.0	38	7.2
Max	78.4	23.98	45.9	8.30	20.08	2.74	142	264	38.8
Mean	27.9	5.46	22.4	6.08	13.10	1.39	18.3	94	19.0
CV (%)	26.1	49.6	37.1	9.3	23.8	32.9	113.2	76.4	35.3
Skew	2.20	3.06	0.34	0.01	0.04	0.46	4.73	1.59	0.46
Kurt	11.14	16.33	-0.37	0.80	-0.57	-0.15	36.25	5.73	1.92

<sup>a</sup> Min, minimum; Max, maximum; CV, coefficient of variation; Skew, skewness; Kurt, kurtosis.

<sup>b</sup> T-Cu, total Cu concentration; A-Cu, available Cu concentration; CEC, cation exchange capacity; SOM, soil organic matter content; TN, total nitrogen concentration; AP, available phosphorus concentration; AK, available potassium concentration; Available ratio, the ratio of available Cu concentration to total Cu concentration, expressed as a percentage.

with a mixture of nitric acid (HNO<sub>3</sub>) and perchloric acid (HClO<sub>4</sub>) (Agricultural Chemistry Committee of China, 1983). Available Cu was extracted with diethylenetriamine penta-acetic acid (DTPA) according to the method described by Lindsay and Norvell (1978) and analyzed by inductively coupled plasma-atomic emission spectroscopy. Available Cu can be extracted by numerous extractants including DTPA, ethylenediaminetetraacetic acid (EDTA), and neutral salts being the most widely used or recommended (Brun et al., 1998; Soil Science Society of China, 1999). The extraction method of DTPA provides more information about metal availability and tends to correlate with metal uptake by plants (Hooda and Alloway, 1994).

### 2.3. Correlation analysis

In this study, correlation analysis was applied to identify the relationships between total Cu concentration, available Cu, Cu availability ratio and selected soil properties (soil pH, SOM, TN, AP, AK and CEC). Also, correlation analysis was performed to assess the relationship between total Cu concentration and available Cu concentration. Spearman non-parametric correlation coefficient was used for variables that were positively skewed. Correlation analysis was performed using SPSS R13.0 for Windows.

### 2.4. Geostatistical analysis

In linear geostatistics, a normal distribution for the variables under study is desirable (Webster and Oliver, 2001; Zhang and McGrath, 2004). To avoid distortion of results and low levels of significance, data transformations are performed on all measured values. Of the numerous data transformation methods, logarithmic transformation is widely applied (Webster and Oliver, 2001). In our study, natural logarithmic transformation was used to normalize the data and reduce skewness. Exponential transformation was used to back-transform the data with all back transformations performed using Version 9.1 of ERDAS IMAGINE (Leica Geosystems, Atlanta, GA).

Geostatistical estimation allows one to predict values at unsampled locations by taking into account the spatial correlation between

estimated and sampled points and minimizing the variance of estimation error and investigation costs (Ferguson et al., 1998; Saito et al., 2005). In recent years, geostatistical methods have been used to effectively assess the spatial variability of soil nutrients and heavy metals (Meuli et al., 1998; Webster and Oliver, 2001; Mueller et al., 2003). The semivariogram, the main component of kriging, is an effective tool for evaluating spatial variability (Boyer et al., 1991; Cahn et al., 1994). The variogram provides a clear description of the spatial structure of variables and provides some insight into possible processes affecting data distribution (Webster and Oliver, 1990; Paz González et al., 2001). In this study, anisotropy of variograms was not found for all data. All semivariograms in isotropic form were fit using a spherical model, exponential model, Gaussian model and linear model. The best-fit model was applied to kriging interpolation. Ordinary kriging was chosen to create the spatial distribution maps of soil Cu after data transformation, using the nearest 16 sampling points and a maximum search distance equal to the range distance of the variable. The resolution of the interpolated grid was 10 m. For a more technical description of kriging and the semivariogram, see Webster and Oliver (2001). Software version 7.0 of GS+ Geostatistics for the Environmental Sciences (Gamma Design Software, Plainwell, MI) was used to perform all the geostatistical computations.

In order to map the distribution patterns of the Cu availability ratio, the ratio was calculated using the modeler function in Version 9.1 of ERDAS IMAGINE by dividing the prediction map of available Cu concentration by the prediction map of total Cu concentration, with both maps being in grid format.

## 3. Results and discussion

### 3.1. Descriptive statistics

A descriptive summary of soil Cu concentration and selected soil properties (SOM, TN, AP, AK content, CEC and pH) are listed in Table 1. The results indicate that total Cu, available Cu, and Cu availability ratio had wide ranges in values. The coefficients of variation (CVs) were 26.1%, 49.6%, and 35.3% for total Cu, available Cu, and Cu availability ratio, respectively. This indicates that available Cu concentration and

**Table 2**  
The non-parametric correlations between total Cu concentration (T-Cu), available Cu concentration (A-Cu), Cu available ratio (A-Cu/T-Cu) and six soil properties.

	T-Cu	A-Cu	SOM	pH	TN	AP	AK	CEC
Cu available ratio	0.40**	0.82**	0.54**	-0.47**	0.48**	-0.07	0.05	0.33**
T-Cu		0.82**	0.64**	-0.30**	0.57**	-0.14*	0.71**	0.86**
A-Cu			0.73**	-0.46**	0.66**	0.03	0.44**	0.64**
SOM				-0.37**	0.87**	0.02	0.36**	0.59**
pH					-0.28**	0.23**	0.04	-0.24*
TN						0.06	0.35**	0.50**
AP							0.23**	0.09
AK								0.64**

SOM, soil organic matter; TN, total nitrogen concentration; AP, available phosphorus concentration; AK, available potassium concentration; CEC, cation exchange capacity.

\*\* Correlation is significant at the 0.01 level (2-tailed).

\* Correlation is significant at the 0.05 level (2-tailed).

Cu availability ratio had greater variation than that of total Cu concentration in the study area. The larger variation of available Cu concentration and Cu availability ratio may be the result of extrinsic factors being more of an influence on these two soil properties than on total Cu concentration. The results also indicate that SOM, TN, AP and AK also had wide ranges and high CVs (>25%) that is a consequence of the high heterogeneity of paddy soil in the study area.

### 3.2. Accumulation status of soil Cu

The background value of Cu at the Zhejiang Province scale is  $17.76 \text{ mg kg}^{-1}$  (Zhejiang Soil Survey Office, 1994). Based on background levels at Zhejiang Province scale, 96.9% of soil samples for total Cu in our study exceeded this baseline concentration. This indicates that Cu accumulation is widely present in agricultural soils of the study area. Based on Chinese Environmental Quality Standard for Soils (GB 15618–1995) (State Environmental Protection Administration of China, 1995), however, there were only two samples having Cu concentrations that exceeded the guideline value for total Cu ( $50 \text{ mg kg}^{-1}$  when soil pH values were less than 6.5, and  $100 \text{ mg kg}^{-1}$  when pH values were greater than 6.5). This indicates that paddy soils in a majority of study area are below Cu contamination levels.

### 3.3. Correlation

To characterize the relationships between total Cu concentration, available Cu concentration, Cu availability ratio, and selected soil properties (soil pH, SOM, TN, AP, AK and CEC), we calculated Spearman non-parametric correlation coefficients for each property (Table 2). The results indicate that total Cu concentration was positively correlated with TN, SOM, AK and CEC with moderate to high correlation ( $r_s = 0.57\text{--}0.86$ ). It is well known that TN is positively correlated with SOM with a high correlation coefficient since most of the Nitrogen is organically bound. In addition, available potassium (AK) is positively correlated with CEC with moderate to high correlation. In this study, there was a strong positive correlation between SOM and TN ( $r_s = 0.87$ ,  $P < 0.01$ ) and moderate positive correlation between AK and CEC ( $r_s = 0.64$ ,  $P < 0.01$ ). This indicates that the statistical correlation between total Cu concentration and TN and AK may arise from the interaction of independent soil properties such as SOM and CEC, since SOM and CEC were two major soil properties that influenced the total Cu distribution in the study area. SOM and TN were also positively correlated with available Cu and Cu availability ratio with moderate correlation coefficients ( $r_s = 0.48\text{--}0.73$ ,  $P < 0.01$ ). Previous studies, however, indicate that Cu is readily chelated with SOM and becomes unavailable (Hodgson et al., 1966; Inaba and Takenaka, 2005) and SOM is negatively correlated with available Cu (Tills and Alloway, 1983; Sakal et al., 1984). The total Cu concentration increases with the SOM content enhance, and only a small proportion of Cu is chelated with SOM. This may explain the positive correlation between SOM and available Cu concentration. CEC was correlated with available Cu concentration with moderately high correlation ( $r_s = 0.64$ ,  $P < 0.01$ ), indicating that CEC was also one of the major soil properties that influenced the distribution of available Cu. The correlation between total Cu concentration, available Cu concentration and CEC indicates that the degree of CEC influence on available Cu concentrations was similar to that influence on total Cu concentration. This may explain why CEC was less positively correlated with the Cu availability ratio ( $r_s = 0.33$ ,  $P < 0.01$ ). Available Cu concentration and Cu availability ratio were negatively correlated with pH with moderately high correlation coefficients ( $r_s = 0.46\text{--}0.47$ ,  $P < 0.01$ ), suggesting that pH was also one of the major soil properties influencing the available Cu concentration and Cu availability ratio. The results of correlation analysis (not listed in Table 2) also indicated that the Cu availability ratio and available Cu concentration were decreased as a function of decreasing pH in acid soils ( $\text{pH} < 6.5$ ) and increased with increasing pH in alkali soils ( $\text{pH} > 7.5$ ). Total Cu concentration was positively correlated with available Cu concentra-

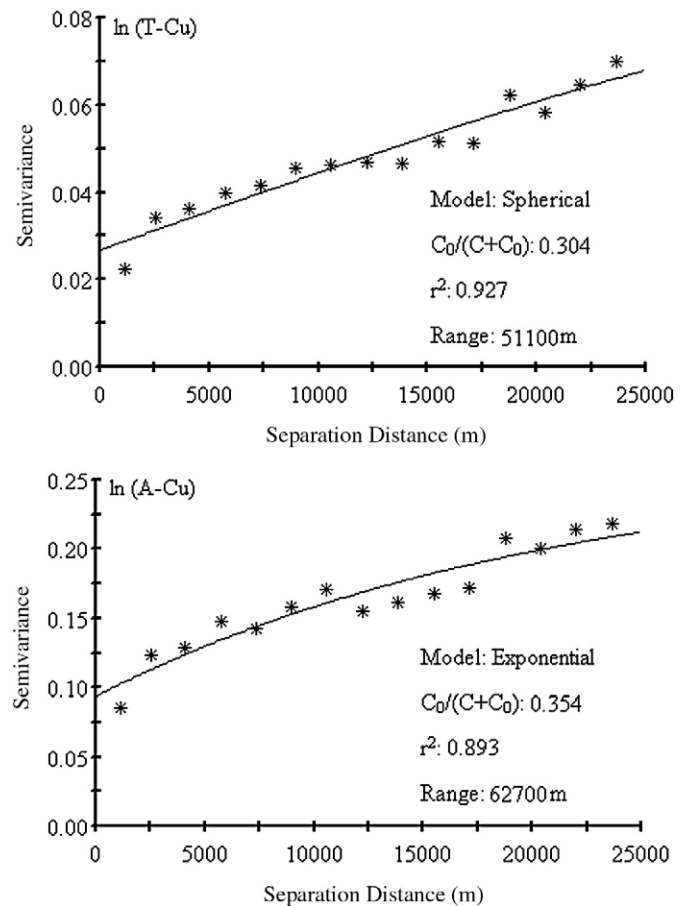


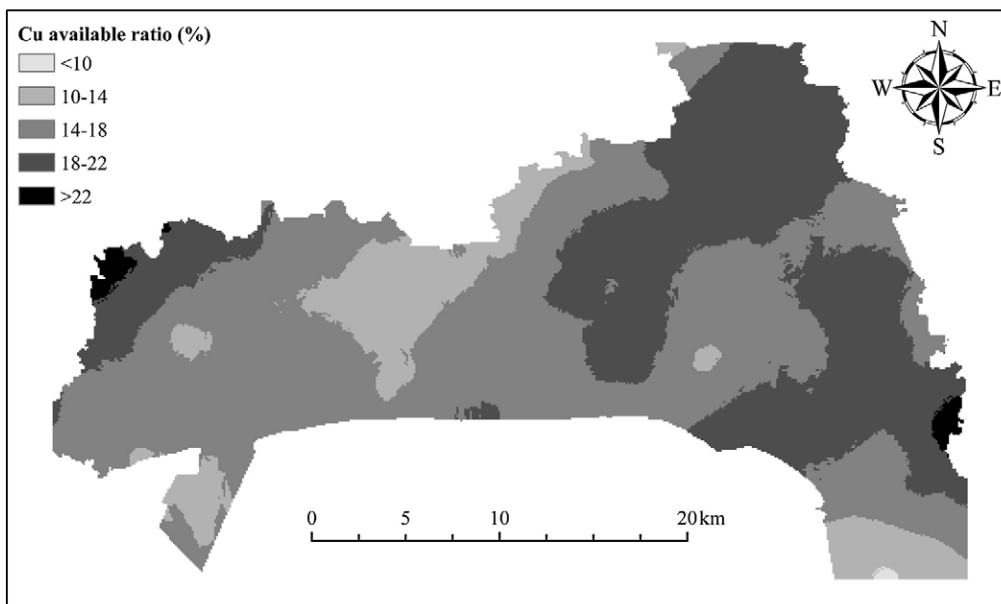
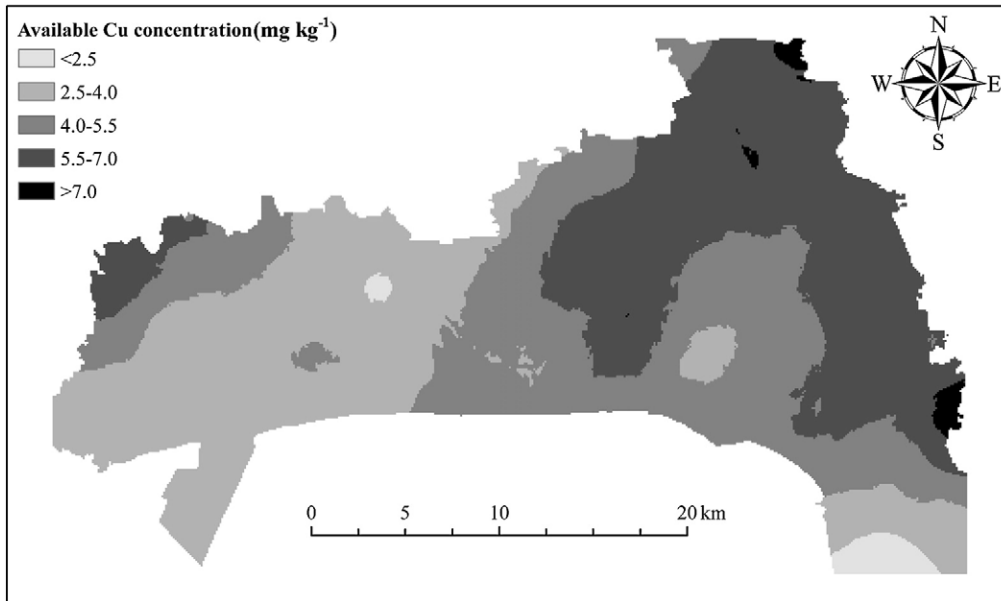
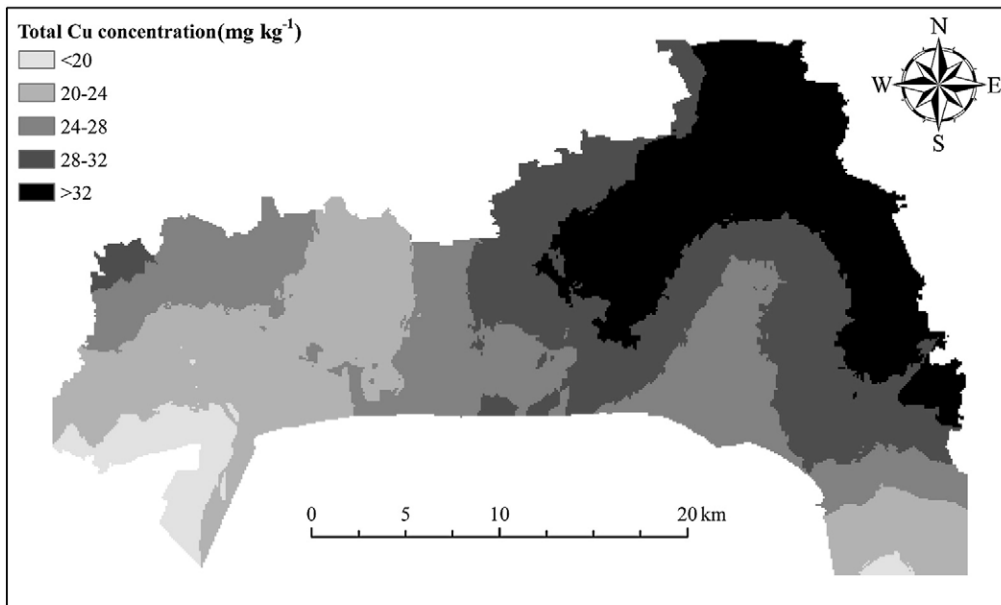
Fig. 2. Experimental semivariograms of natural logarithmic total Cu ( $\ln(T\text{-Cu})$ ), natural logarithmic available Cu ( $\ln(A\text{-Cu})$ ), with fitted models and their parameters.

tion with correlation coefficient of 0.82, indicating that available Cu concentration increases with total Cu concentration. A statistical correlation between Cu availability ratio and total Cu concentration may come from the interaction of independent soil properties such as SOM since total Cu was moderately positively correlated with SOM.

In the study area, paddy fields were in a dry phase during the period from October to March, and in a flooding phase during the period of May to August. In general, the rice was harvested during later October or early November. All the soil samples were collected several days after the paddy rice was harvested. Hence, the results of this study only reflect Cu availability when paddy fields were in the dry phase. Further study is needed in order to elucidate Cu availability when paddy fields are in the flooding phase under anaerobic conditions.

### 3.4. Spatial structure and spatial distribution

Total Cu and available Cu were transformed to the natural logarithmic form before geostatistical analysis as they exhibited high kurtosis and skewness. Soil heavy metals generally have spatial structure, including high spatial autocorrelation. In this study, geostatistical methods were used to analyze this spatial structure and to spatially estimate copper concentrations in unsampled areas. The semivariogram and the fitted models for total Cu concentration and available Cu concentration are presented in Fig. 2. The parameters of the two semivariograms are also presented in Fig. 2. The fitted models were spherical for total Cu concentration and exponential for available Cu concentration. The Nugget/Sill ratio was the criterion we used to classify the spatial dependence of variables. Ratio values lower than 25% and higher than 75% corresponded to strong and weak



spatial dependency, respectively, while the ratio values between 25 and 75% corresponded to moderate spatial dependence (Cambardella et al., 1994). 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 Nugget/Sill ratios of the two models were between 25 and 75%, indicating that both logarithmic transformed total Cu concentration and logarithmic transformed available Cu concentration exhibited moderate spatial dependency. Their spatial dependence may be attributed to both intrinsic factors such as soil properties and extrinsic factors such as anthropic (or human-induced) activities. Range value is a measure of the spatial extension within which autocorrelation exists (Webster and Oliver, 1990). The ranges were 51.1 km for total Cu and 62.7 km for available Cu. This suggests that the spatial correlation structure of available Cu concentration had a longer range than that of total Cu concentration and total Cu concentration was more vulnerable to the influences of extrinsic factors such as anthropic activity than that of available Cu concentration.

In order to generate the distribution patterns of total Cu concentration and available Cu concentration, ordinary kriging interpolation was used (Fig. 3). The spatial distribution maps of total Cu concentration and available Cu concentration exhibited similar distribution trends with high concentrations in the northeastern region and low concentrations in the southwestern region of the study area. The spatial distribution maps of Cu availability ratio, estimated by dividing the predicted available Cu concentration by the predicted total Cu concentration, showed a distribution trend with the highest ratios in the northeast region and lower ratios in the central region of the study area. There were some differences in distribution trends between Cu availability ratio and total Cu concentration and available Cu concentration. This indicates that the Cu availability ratio was influenced by a different set of environmental factors than that of total Cu concentration and available Cu concentration.

Based on the results of correlation analysis, we found that soil properties such as SOM, TN and CEC have the potential as useful auxiliary variables for improving the precision and reliability of total and available Cu concentration predictions. Available Cu and SOM have the potential as useful auxiliary variables for improving the precision and reliability of the Cu availability ratio. Though considered, we did not employ cokriging for the spatial prediction of Cu concentrations. Cokriging with auxiliary variables would not significantly improve the prediction precision because of the auxiliary variables that were not exhaustively sampled, and cokriging would have been less valid than ordinary kriging for spatial prediction given the nature of our dataset.

#### 4. Conclusions

Total Cu concentration, available Cu concentration and Cu availability ratio had wide range and high variability. Cu accumulation was widely present in paddy fields of the study area in comparison to the background levels at Zhejiang Province scale. Copper in the paddy field soils for a majority of the study area, however, was at concentrations less than soil contamination levels. Thus, soils were considered unpolluted by copper according to the Chinese Environmental Quality Standard for Soils. The concentrations of total Cu and available Cu in paddy fields had a moderate spatial dependency and relatively long range.

SOM and CEC were two major soil properties that influenced the variability of total Cu concentration and available Cu concentration. In addition, SOM and pH were two soil properties that influenced the variability of the Cu availability ratio. Total Cu and available Cu concentrations had similar distribution trends with the highest concentrations in the northeast region and lowest concentrations in

the southwest regions of the study area. The copper availability ratio had a spatial distribution trend with the highest ratios in the northeast region and lowest ratios in the middle region of the study area.

#### Acknowledgements

This research was funded in part by the International Cooperation Program of the Chinese Ministry of Science and Technology (project no. 2006DFA91940) and the National Basic Research Priorities Program (973 Program) (2002CB410810). We extend our great appreciation to two anonymous reviewers and Dr. Alfred Hartemink, editor-in-chief of *Geoderma*, for their comments. We also express our appreciation to Dr. Stephen D. DeGloria, Cornell University, for his contributions to this manuscript. We gratefully acknowledge all of our colleagues who collected and analyzed the soil samples.

#### References

- Agricultural Chemistry Committee of China, 1983. *Conventional Methods of Soil and Agricultural Chemistry Analysis* (in Chinese). Science Press, Beijing, pp. 70–165.
- Alloway, B.J., 1995. *Heavy Metals in Soils*. Blackie Academic and Professional, London.
- Amini, M., Khadem, H., Afyuni, M., Abbaspour, K.C., 2005. Variability of available cadmium in relation to soil properties and landuse in an arid region in central Iran. *Water, Air, and Soil Pollution* 162, 205–218.
- Boojar, M.M.A., Goodarzi, F., 2007. The copper tolerance strategies and the role of antioxidative enzymes in three plant species grown on copper mine. *Chemosphere* 67, 2138–2147.
- Boyer, D.G., Wright, R.J., Feldhake, C.M., Bligh, D.P., 1991. Soil spatial variability in steeply sloping acid soil environment. *Soil Science* 161, 278–287.
- Brun, L.A., Maillet, J., Richarte, J., Herrmann, P., Pemy, J.C., 1998. Relationships between extractable copper, soil properties and copper uptake by wild plants in vineyard soils. *Environmental Pollution* 102, 151–161.
- Cambardella, C.A., Moorman, T.B., Nocak, J.M., Parkin, T.B., Karlen, D.L., Turco, R.F., Konopka, A.E., 1994. Field-scale variability of soil properties in central Iowa soils. *Soil Science Society of American Journal* 58, 1501–1511.
- Cahn, M.D., Hummel, J.W., Brouer, B.H., 1994. Spatial analysis of soil fertility for site-specific crop management. *Soil Science Society of American Journal* 58, 1240–1248.
- Demirevska-Kepova, K., Simova-Stoilova, L., Stoyanova, Z., Hölzer, R., Feller, U., 2004. Biochemical changes in barley plants after excessive supply of copper and manganese. *Environmental and Experimental Botany* 52, 253–266.
- Ferguson, C.C., Darmendrail, D., Freier, K., Jensen, B.K., Kasamas, H., Urzelai, A., Vegter, J. (Eds), 1998. *Risk assessment for contaminated sites in Europe*. LQM Press, Nottingham, pp. 135–146. Scientific Basis.
- He, M., Wang, Z., Tang, H., 1997. Spatial and temporal patterns of acidity and heavy metals in predicting the potential for ecological impact on the Le An river polluted by acid mine drainage. *Science of the Total Environment* 206, 67–77.
- Hodgson, J.F., Lindsay, W.L., Trier Weiler, J.F., 1966. Micronutrient cation complexing in soil solution. II. Complexing of zinc and copper in displaced solutions from calcareous soils. *Soil Science Society of American Proceedings* 30, 723–726.
- Hooda, P.S., Alloway, B.J., 1994. The plant availability and DTPA extractability of trace metals in sludge-amended soils. *Science of the Total Environment* 149, 39–51.
- Inaba, S., Takenaka, C., 2005. Changes in chemical species of copper to brown forest soil in Japan. *Water, Air, and Soil Pollution* 162, 285–293.
- Jeffrey, G.W., Robert, J.Z., 1999. Mapping soil micronutrients. *Field Crop Research* 60, 11–26.
- Jenne, E.A., 1968. Controls on Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides. *Advanced Chemistry* 73, 337–387.
- Jung, M.C., 2001. Heavy metal contamination of soils and waters in and around the Imcheon Au–Ag mine, Korea. *Applied Geochemistry* 16, 1369–1375.
- Kabata-Pendias, A., Pendias, H., 2001. *Trace Elements in Soils and Plants*. CRC, Boca Raton.
- Kim, H.T., 2005. *Soil Sampling, Preparation, and Analysis*. CRC, Florida, pp. 260–283.
- Lee, C.S., Kao, M.M., 2004. Distribution of forms of heavy metals in soils contaminated by metallurgical smelter emissions. *Journal of Environmental Science and Health* 39 (3), 577–585.
- Lexmond, T.M., van der Vorm, P.D.J., 1981. The effect of pH on copper toxicity to hydroponically grown maize. *Netherlands Journal of Agricultural Science* 29, 217–238.
- Lindsay, W.L., Norvell, W.A., 1978. Development of a DTPA soil test for zinc, iron, manganese and copper. *Soil Science Society of America Journal* 42, 421–428.
- Ma, L.Q., Rao, G.N., 1997. Chemical fractionation of cadmium, copper, nickel, and zinc in contaminated soils. *Journal of Environmental Quality* 26, 259–264.
- Mantovi, P., Bonazzi, G., Marmiroli, N., 2003. Accumulation of copper and zinc from liquid manure in agricultural soils and crop plants. *Plant and Soil* 250, 249–257.
- McBride, M.B., Richards, B.K., Steenhuis, T., Russo, J.J., Sauve, S., 1997. Mobility and solubility of toxic metals and nutrients in soil fifteen years after sludge application. *Soil Science* 162, 487–500.

**Fig. 3.** The prediction map of total Cu concentration by ordinary kriging, available Cu concentration by ordinary kriging, and Cu available ratio by method of the predicted available Cu concentration divided by the predicted total Cu concentration, respectively.

- Meuli, R., Schulin, R., Webster, R., 1998. Experience with the replication of regional survey of soil pollution. *Environmental Pollution* 101, 311–320.
- Micó, C., Recatalá, L., Peris, M., Sánchez, J., 2006. Assessing heavy metal sources in agricultural soils of an European Mediterranean area by multivariate analysis. *Chemosphere* 65, 863–872.
- Mizuno, N., Kamada, K., 1982. Method of judging copper deficiency from the concentration of soluble copper in the soils and copper: iron ratio in wheat plants. *Soil Science and Plant Nutrition* 28, 27–36.
- Moreno, J.L., Garcia, C., Hernandez, T., Ayuso, M., 1997. Application of composted sewage sludges contaminated with heavy metals to an agricultural soil. *Soil Science and Plant Nutrition* 43, 565–573.
- Mueller, T.G., Hartsock, N.J., Stombaugh, T.S., Shearer, S.A., Cornelius, P.L., Barnhise, R.L., 2003. Soil electrical conductivity map variability in limestone soil overlain by loess. *Agronomy Journal* 95, 496–507.
- Paz González, A., Taboada Castro, M.T., Vieira, S.R., 2001. Geostatistical analysis of heavy metals in a one-hectare plot under natural vegetation in a serpentine area. *Canadian Journal of Soil Science* 81 (4), 469–479.
- Pietrzak, U., McPhail, D.C., 2004. Copper accumulation, distribution and fraction in vineyard soils of Victoria, Australia. *Geoderma* 122, 151–166.
- Prasad, B.R., Basavaiah, S., Subba, R.A., Subba, R.I.V., 1984. Forms of copper in soils of grape orchards. *Journal of the Indian Society of Soil Science* 32, 318–322.
- Qin, S.C., Luo, Y.M., Huang, C.Y., Wu, Z., Zhu, L.C., 1992. Study on 'Blind-Ear' – copper deficiency symptoms in wheat on subtropical hill soils. *Pedosphere* 2, 85–92.
- Saito, H., McKenna, A., Zimmerman, D.A., Coburn, T.C., 2005. Geostatistical interpolation of object counts collected from multiple strip transects: ordinary kriging versus finite domain kriging. *Stochastic Environmental Research and Risk Assessment* 19, 71–85.
- Sakal, R., Singh, A.P., Singh, B.P., Sinha, R.B., 1984. Evaluation of some chemical extractants for predicting response to wheat grown in pots in sub-Himalayan soils. *Journal of Agricultural Science* 102, 659–666.
- Shi, J.C., Xu, J.M., Huang, P.M., 2008. Spatial variability and evaluation of status of micronutrients in selected soils around Taihu Lake, China. *Journal of Soils and Sediments* 8, 415–423.
- Shuman, L.M., 1985. Fractionation method for soil microelements. *Soil Science* 140, 11–22.
- Shuman, L.M., 1988. Effects of organic matter on the distribution of manganese, copper, iron, and zinc in soil fractions. *Soil Science* 146, 192–198.
- Shuman, L.M., 1991. Chemical forms of micronutrients in soils. In: Mortvedt, J.J., Cox, F.R., Shuman, L.M., Welch, R.M. (Eds.), *Micronutrients in Agriculture* (2nd edn). Soil Science Society of America, Madison, Wisconsin, pp. 113–114.
- Soil Science Society of China, 1999. *Analysis Methods for Soil and Agricultural Chemistry* (in Chinese). China Science and Technology Press, Beijing.
- State Environmental Protection Administration of China, 1995. *Chinese Environmental Quality Standard for Soils* (GB 15618-1995).
- Sterckeman, T., Douay, F., Baize, D., Fourrier, H., Proix, N., Schwartz, C., 2004. Factors affecting trace element concentrations in soils developed on recent marine deposits from northern France. *Applied Geochemistry* 19, 89–103.
- Tills, A.R., Alloway, B.J., 1983. An appraisal of currently used soil tests for available copper with reference to deficiencies in English soil. *Journal of the Science of Food and Agriculture* 34, 1190–1196.
- Tisdal, L.S., Nelson, W.L., Beaton, J.D., Havlin, J.L., 1993. *Soil Fertility and Fertilizers*, 5th edn. Macmillan, New York, NY.
- Wang, G., Su, M.Y., Chen, Y.H., Lin, F.F., Luo, D., Gao, S.F., 2006. Transfer characteristics of cadmium and lead from soil to the edible parts of six vegetable species in southeastern China. *Environmental Pollution* 144, 127–135.
- Webster, R., Oliver, M.A., 1990. *Statistical Methods in Soil and Land Resource Survey*. Oxford University Press, London.
- Webster, R., Oliver, M.A., 2001. *Geostatistics for Environmental Scientists*. Wiley, New York.
- Zhang, C., McGrath, D., 2004. Geostatistical and GIS analyses on soil organic carbon concentrations in grassland of southeastern Ireland from two different periods. *Geoderma* 119, 261–275.
- Zhang, X.L., Gong, Z.T., 2004. A pedodiversity pattern: taxonomically established soil orders in China. *Journal of Geographical Sciences* 14, 52–56 suppl.
- Zhejiang Soil Survey Office, 1994. *Zhejiang Soils* (in Chinese). Zhejiang Technology Press, Hangzhou, pp. 556–562.