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

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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^2. 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 ($r=0.64$–0.82), and Cu availability was directly correlated with SOM, pH and Cu concentration with moderate to high positive correlation ($r=0.47$–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.

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 phosphor; 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.

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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^2. 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.

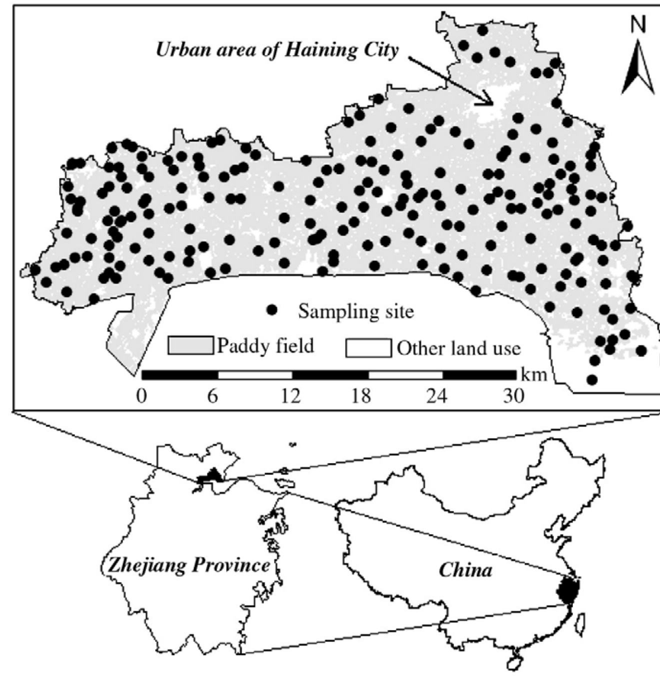

Fig. 1. The location of study area and distribution of sampling sites.

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 hand-held 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^{-1} 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 $H_2SO_4 + H_2O_2$ digestion. Available phosphorus (AP) was extracted using 0.03 mol L^{-1} NH_4F–0.025 mol L^{-1} HCl or 0.5 mol L^{-1} $NaHCO_3$ (based on pH values), and analyzed using the molybdenum-blue method. Available potassium (AK) was extracted using 1 mol L^{-1} NH_4OAc 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